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Optimization and characterization of solution-processed fluoropolymer coatings.

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OPTIMIZATION AND CHARACTERIZATION OF SOLUTION-PROCESSED FLUOROPOLYMER COATINGS

A Dissertation Presented

by

MEREDITH L. WHITE

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To Mom, Dad, Deanna, Natalie, and Matt

ACKNOWLEDGEMENTS

I must admit, my time spent at UMass trying to accomplish this dissertation work has been sometimes tenuous. Some personal relationships suffered as a result of my uncertainty in myself with regard to the task at hand. I value the science and research lessons I learned from faculty and colleagues at UMass Polymer Science Dept., but ultimately, I'm indebted to some of these individuals for what they taught me about myself. I learned that I could overcome self-doubt and that I have the strength and confidence in myself to do so in the future.

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ABSTRACT

CHARACTERIZATION AND OPTIMIZATION OF SOLUTION-PROCESSED FLUOROPOLYMER COATINGS

FEBRUARY 1998

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New grades of fluoropolymers are available from DuPont that have been designed to relieve some of the processing problems associated with these materials. By nature, Teflon® is very viscous in the melt state, and only high energy processes allow material processing. These new grades of fluoropolymers are the first to be dissolvable, by perfluorinated solvents, and have opened up a whole new field of solution processing. It has been the aim of this work to investigate this new field of research.

New solution processing techniques have been developed to create strong well-adhered coatings of fluoro-ethylene-propylene (FEP) copolymers to various substrate materials, ranging from 50nm to 100μm. By observing and exploiting upper and lower critical solution temperatures, solutions of concentrations up to 15 wt. % have been achieved, well above the 1 wt % solutions produced at DuPont. This enabled the

formation of FEP coatings in one step, rather than attempting multiple layers to achieve greater thickness.

Due to the fact that these are new experimental grades of FEP, physical properties have been investigated by thermal and x-ray analysis. In terms of coating properties, the coatings have shown remarkable adhesion properties that are measured by a unique self decohesion test approach, developed in this laboratory. In order to define optimal uses for these materials as coatings, barrier properties have been measured. Permeability tests have been conducted using carbon dioxide and air as the permeant and Atlas cell corrosion tests have been run to compare the corrosion resistance among the copolymers being studied. Mechanical properties have also been characterized by holographic interferometry, which measures the in-plane residual stresses, and Instron testing, for tensile properties of the films.

In an effort to improve coating quality, while taking advantage of the solution media, sol-gel reaction schemes have been modified by DuPont researchers to be carried out in these perfluorinated solvents in the presence of the dissolved FEP. The result would be the formation of an SiO_2 network around the FEP molecules, producing a nano-composite material. This and other on-going work, in the area of coupling agents or adhesion promoters, is being done to investigate the effects on adhesion and other properties mentioned above.

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INTRODUCTION AND BACKGROUND

Introduction

New grades of fluoropolymers are available from DuPont that have been designed to relieve some of the processing problems associated with Teflon® PTFE (polytetrafluoroethylene) and FEP (fluoro-ethylene-propylene) materials. By nature, PTFE and FEP are very viscous in the melt state, and only high energy processes allow material processing. These new grades of fluoropolymers are the first to be dissolvable, by perfluorinated solvents, and have opened up a whole new field of solution processing. It has been the aim of this work to investigate this new field of research.

Teflon® fluoropolymers have become widely known in the materials industry for their very low surface energy and that they are inert to most industrial chemicals and solvents. The name actually encompasses many different forms of perfluorinated polymers. In general, the materials have high thermal stability over a wide temperature range and low dielectric constants, as well, which make them outstanding in engineering applications when coupled with the above properties. As a result, fluoropolymers have found application not only in processing components such as tubing, mold release agents, and liners, but also, in labware and insulation for cables and wires. In addition, the PTFE and FEP have low refractive indices, which can make them useful as optical materials.

All of the above characteristics are very desirable for certain specialty applications, but the usage has been limited by the processing problems. Therefore, this

for Teflon® FEP. Not only does this open up the option to solvent cast thin films and coatings of FEP, but also, by having a solution media, new solution chemistry or mixing schemes are possible to modify and hopefully improve the coating characteristics. The solvent incorporation may also enable facile fiber spinning capabilities where, before its been very difficult due to the high melt viscosities. So this work is primarily an investigation of the new processing available for the new fluoropolymers introduced. The resultant properties of the fluoropolymers made by solution processing are also investigated and compared to the similar materials made by existing commercial technology. Also, further work has been done in composite technology to improve upon known weaknesses in the material, i.e. abrasion resistance and adhesion.

Background

History of Teflon® Products

Teflon® PTFE

The first polymer of tetrafluoroethylene (TFE - CF_2=CF_2) was discovered by Plunkett in 1938 and patented in 1941 when TFE gas was found to have polymerized inside its tank. [1] Later, a polymerization scheme was developed to carry out the high energy reaction in an aqueous suspension, initiated radically by persulfate. PTFE (polytetrafluoroethylene -(CF_2CF_2)-) is a linear fluorocarbon material which exhibits a high degree of crystallinity (95-98%) [2]. The crystallinity is so high that lower molecular weight PTFE is too brittle for the applications for which it is intended. In order to enhance the toughness, researchers attempted to either maintain higher molecular weight materials, which would allow molecular linkages between crystallites,

or decrease the degree of crystallinity through polymerization with a comonomer.[3] So the PTFE homopolymer that is available is of very high molecular weight (~10^6-10^7) and the melt viscosity is very high (~10^{10} - 10^{11} poise) [4].

PTFE processing

In order to process a material of such intractability in the melt state, new dry processing techniques were in order. To mold PTFE, the granular resin is normally finely ground and compressed into a handleable preformed mold while still below 100°C. Subsequent sintering (~380°C) is required to obtain the final molded product, which can be done inside the mold at autogenous pressure or with the mold removed to sinter it freely. Precision articles may need subsequent machining to arrive at the desired tolerances.

Pipes or rods of PTFE are formed in a very high energy ram extrusion process where to begin with a small charge of PTFE powder is preformed by a reciprocating ram and sintered in a long tube. [2, 5] Subsequent melted and compacted powder charges are rammed into the previous form and are fused to it by sintering. This process is repeated until the desired length is achieved. The tube is normally heated by resistance heating which must be carefully balanced to minimize the thermal expansion and high friction forces developed in the tube. The force applied in the ram is very large to overcome the resistance of these forces.

The paste extrusion process was developed which allows extrusion of the PTFE, which is otherwise impossible to flow in the melt. [6] This entails the mixing of the PTFE fine powder with 16-25 wt % of a lubricant, like naptha or kerosene, to obtain a uniform

distribution. The mixture is then shaped into a preform with low pressure and then pushed through an extruder at ambient temperature. Care must be taken in handling and extruding the fine powder because it is sensitive to shear. After the extrusion, the lubricant must be removed by evaporation, leaving a porous PTFE article. To solidify, it must finally be sintered at about 380°C.

PTFE is also processed by means of an aqueous dispersion. [7] Here, 30-60 wt % PTFE and surfactant are suspended in an aqueous medium. It can be used to apply PTFE coatings to various substrates by standard methods, followed by drying to remove the water and subsequent sintering to coalesce the powder particles. Also, these dispersions are used to spin fibers of PTFE. This requires mixing the dispersion with a matrix forming material, spinning the fiber into a coagulation bath, heating the fiber to remove the matrix forming material and finally sintering and drawing the fiber to achieved the desired properties.

All of these processing methods are very energy intensive. In addition, since all the processing must be done with powder and possibly a lubricant, high temperatures are required in a post-processing step to coalesce the powder and remove the lubricant. In many cases, especially in dispersion coating applications, the final product of PTFE is still very porous and optimal properties, such as low permeability and high corrosion resistance, are not achieved.

PTFE properties

PTFE has unique engineering properties due to the large fluorine atoms, which collectively act as a protective sheath along the carbon backbone and make the polymer

completely nonpolar. This protective sheath prevents attack from most industrial solvents and harsh environments. The surface energy is very low resulting in a non-stick surface with a low coefficient of friction. This property can be attributed to the non-polarity and high electronegativity of the fluorine which results in weak van der Waals attraction forces. The high degree of crystallinity and very high melting point (327°C) lead to a broad service temperature range, even dipping into cryogenic environments. This phenomenon can be traced back to the fact that the C-F bond is relatively short and very strong resulting in high thermal and chemical stability [8]. Also, the fluorocarbon has a low dielectric constant of 2.0 that fosters excellent insulating properties. The material has one of the lowest refractive indices, 1.3, exhibited by polymer materials as well [4]. However, the non-polarity leads to a situation where there are very little intermolecular interactions within the material itself, which results in higher creep and ductility than most engineering polymers. The tensile strength is average for a thermoplastic and falls in the range of 7-28 MPa depending on the preparation.

Teflon® FEP

As mentioned above, in order to get tougher fluoropolymer products, one solution was to polymerize it with a comonomer to reduce the crystallinity. In 1957, Bro and Sandt published a patent teaching a method of synthesizing copolymers of TFE and hexafluoropropylene (HFP) that are melt-extrudable perfluorocarbon polymers.[9] They realized that, although HFP does not homopolymerize under the PTFE reaction conditions, it does copolymerize with TFE under these conditions. Small amounts of HFP were added to the PTFE polymerization and Bro and Sandt report copolymer

products with specific infrared (IR) ratios (ratio of HFP present to the total absorbance spectrum) of anywhere from 1.5 to 6. [9] They claim that, by using a multiplication factor of 4.5, the IR ratio is equivalent to the weight percent HFP present. Upon conversion, this corresponds to claims of achieving 4.6 - 19.8 mol % HFP, while 15.6 mol % was the highest reported by example. Since the HFP does not homopolymerize under the aqueous radical reaction conditions used, the TFE/HFP copolymer, or fluoro-ethylene-propylene (FEP), is believed to be mostly random with little to no repeated units of the HFP which could lead to blockiness. (See Figure 1.1.)

FEP processing

Three grades of FEP have become commercially available from DuPont in the form of Teflon® FEP 100, Teflon® FEP 140, and Teflon® FEP 160. They differ in the amount of HFP present with FEP 100 being the most processable and having the highest HFP content at 13 mole %. [10] Since the HFP is mostly randomly substituted into the backbone at this comonomer loading level, the FEP copolymer retains many of the same properties of the homopolymer but has the desired lower degree of crystallinity due to the bulky CF_3 pendant groups in the HFP unit. This lower degree of crystallinity corresponds to a lower melt viscosity in the range of 4×10^4- 1×10^5 poise. [9] This lower crystallinity corresponds to a lower melting temperature which also aids the processability. The processability is enhanced for the copolymer compared to PTFE,

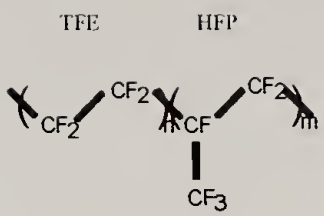


Figure 1.1: Structure of Fluoro-ethylene-propylene (FEP)

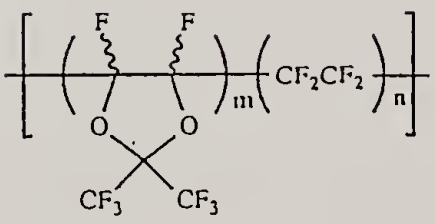


Figure 1.2: Structure of Teflon® AF

however these commercial grades are still relatively difficult to process by standard extruding conditions compared to other thermoplastics [2].

FEP properties

The FEP copolymers described above retain all of the physical properties of the PTFE, like low surface energy, refractive index and dielectric constant. The only properties that are notably changed are the thermal properties, where the melting point drops to 260°C, and the melt viscosity, which drops five orders of magnitude to $\sim 10^5$ poise. The tensile strength is not dramatically changed for FEP which still falls in the range of 20-31 MPa. [2]

Applications

Most of the applications for these fluoropolymers are in areas where their unique combination of properties can be exploited. Wire and cables are coated by both PTFE and FEP in order to provide electrical insulation with high temperature capabilities and non-flammability. Pumps, pipes, engines and tanks are lined with both polymers to take advantage of its low friction and chemical inertness. Also coatings are made onto surfaces where nonstick properties are desirable, as in bakeware and molds. Because of the toughness exhibited over such a wide temperature range, these fluoropolymers are used in making gaskets and o-rings and belts, as well.

The polymers have had some inherent difficulties in certain applications where their properties would be of tremendous use. For example, PTFE does not adhere well to many substrate materials by melt processing, due to the low surface energy and non-wetting characteristics. Adhesion promoters or substrate surface modifications are

required to form coatings. The surface modifications can be quite intense, like sand blasting and acid etching, to enable mechanical interlocking as the primary mechanism of adhesion. Sakamaki et al. describe a process by which the powder PTFE is combined with a fine-powdered polyimide and a filler.[11] They are applied to substrates from a suspension and sintering thereafter. This technique, combined with substrate sand blasting, is similar to what is used in the bakeware industry. Thin films can be applied as coatings as described earlier, however, the drying step does not consistently remove the surfactants required to stabilize the dispersion.[12] Even if it is removed, after the carrier is dried out, it leaves a very porous material that sintering does not appreciably change. Therefore, the thin coatings achievable do not provide the desired barrier properties. The fluoropolymer coating techniques available today are far from optimizing the nature of these fluoropolymers.

Another general weakness of these materials is the abrasion resistance. Both PTFE and FEP have lower tensile strength, abrasion resistance and creep resistance than most other engineering plastics, as mentioned previously. This has really proven to be detrimental in coating applications where the coating is supposed to be providing a barrier to harsh environments for the substrate.

New Materials

Newer fluoropolymer materials have been developed to pinpoint specific areas of application. For instance, Teflon® AF, which is a copolymer of TFE and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, has the lowest refractive index of any

polymer material. [13] (See Figure 1.2) It is completely amorphous and is available in two grades, AF 1600 and AF 2400. They have different glass transition temperatures of 160°C and 240°C, respectively. It has been found that these amorphous fluoropolymers have limited solubility in perfluorocarbon solvents as well. The applications for Teflon® AF materials so far are in pellicles and antireflective coatings. [14, 15] The ability to solution process these materials is a huge advantage when it comes to making the thin films required for anti-reflectivity.

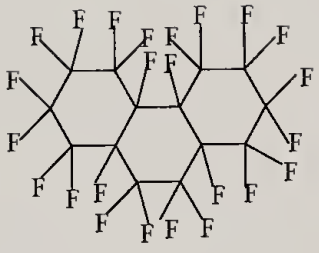
Also, Chapman and Anolick have developed new TFE/HFP copolymers that contain higher contents of the HFP. [16, 17] Originally, Bro and Sandt reported copolymers of TFE and HFP with an HFP index, or HFPI, from specific IR ratio, of 1.5 to 6. [9] This supposedly, corresponds to a range of 4.6 to 19.8 mole %, however, this calculation is questionable due to inconsistencies in the reported calculation in Chapman's patent background. [16] Khan in U.S. Pat. No. 4,381,384 reports an HFPI of 9.5 which depending on which calculation is used, could be 20 or 33 mole %, with the highest actual example reported as 5.4 mol %. Chapman reports the ratios in HFPI index as well, being anywhere from 6.4 to 9. Anolick provided the first comprehensive treatment of the indexing, reporting mole percentages based on ^{19}F NMR. Anolick achieved 35-50 mol % HFP in the TFE/HFP copolymers.[17]

This work is based on two experimental grades of the Teflon® FEP with 25 and 50 mole percent HFP, designated SF-25 and SF-50, respectively. These new polymers were prepared by DuPont researchers, according to the procedure described by Chapman, to be able to dissolve the copolymer for the first time and open up new processing schemes and applications. It turns out that the SF-25 and SF-50 have limited

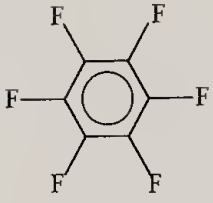
solubility, in various perfluorinated solvents, in certain instances, more than Teflon®AF. At the onset of this investigation SF-25 was the only experimental copolymer available, and the maximum solution concentration that could be achieved at DuPont was 1.6 wt % solids in PP11. Based on work now accomplished in this laboratory, maximum concentrations of 12 wt % and 9 wt % are achieved for SF-25 and SF-50, respectively. The advantage of the new FEP over AF materials is that these polymers are semi-crystalline and behave like commercial FEP. Figure 1.3 shows a group of the most successful solvents utilized for these new fluoropolymers.

These experimental grades of the FEP are chemically very similar to the commercial FEP's available. However, thermal properties and crystallinity are very much changed by the higher ratio of HFP present. At present, the SF-25 can be manufactured in the commercial reactors, whereas, the SF-50 reacts too slow due to the added nonreactive HFP and is manufactured by lab scale.

PP11



HFB



FC-40

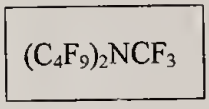


Figure1.3: Structures of Fluoropolymer solvents

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CHAPTER 2

NEW FLUOROPOLYMERS IN SOLUTION

Introduction

In an effort overcome the insolubility of fluoropolymers and possibly aid in the polymer characterization, the solubility of PTFE and FEP have been investigated by other researchers. Originally, a 1950 patent reported the plasticization of 1-2% PTFE at 290-310°C in perfluorokerosenes and other perfluorinated oils. [1] Smith and Gardner later calculated the solution thermodynamics of PTFE in perfluorocarbons based on a Flory-Huggins approach and predicted that a larger melting point depression will occur for solvents of lower molecular weights. [2] However, due to the lower boiling points expected for lower molecular weight perfluorocarbon solvents, they predicted solubility would not be obtained at ambient pressures. Tuminello et al. then ran physical experiments in enclosed vessels (higher pressures) using a specially prepared low molecular weight PTFE to expand on Smith and Gardner's predictions. [3] They found that for autogenous pressures, solvents with critical temperatures above 377°C were the only solvents that actually dissolved the PTFE. These solvents included perfluorodecahydrophenanthrene, or Flutec® PP11, available commercially from BNFL Fluorochemicals Ltd., and its oligomer, a by-product of the manufacture of the PP11, both shown in Figure 2.1.

This high temperature and higher pressure approach led to the investigation of fluoropolymers' solubility in supercritical fluids (SCFs), like low boiling halocarbons and

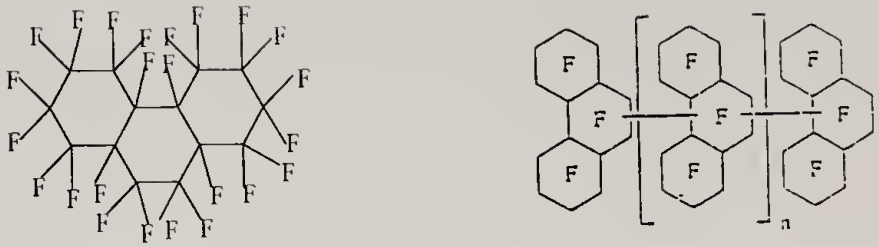
eventually CO_2. [4, 5] [6] The study with low boiling halocarbons (ref. 4), like Freon® 113 and perfluorodecalin, yielded concentrations of less than 1 wt % PTFE. An FEP with 19.3 mole % HFP was introduced in refs. 4 and 5, which was investigated at very high temperatures and pressures and weight concentrations up to 17% in CO_2. While reportedly showing solubility for higher concentrations, the nature of the experiment does not lend to simple subsequent processing.

Solubility Study of New FEP Copolymers

This study focuses on the miscibility of the straight commercial solvent , Flutec PP11, with new copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), highlighted in Figure 2.2. Varying degrees of miscibility are achieved at relatively low temperatures and ambient pressures, for the different fluoropolymers under investigation, and this will be the primary focus of the following solution behavior study. The key parameter to the solubility for the new polymers is that they have higher HFP contents than FEP's that have been available to date, such as the Teflon® FEP 100 in Figure 2.2.

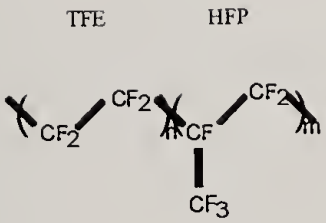
SF-25

At the onset of this thesis, there was a procedure described by the initial investigators as to how to form solutions of the new soluble fluoropolymer, which was only SF-25, at the time. It was supplied in the form of a powder along with the Flutec® PP11 solvent by Jim Fitzgerald and Dr. Charles Stewart from du Pont de Nemours Co.. The procedure prescribed for solution formation was to combine the two components at



$B_p = 215°C$

Figure 2.1. Flutec PP11 and its oligomer



Polymer	m (% HFP)
PTFE	0
FEP100	13
SF-25*	25
SF-50*	50

Figure 2.2: Structures and copolymer content - *new grades from DuPont

room temperature, and heat and stir to 175°C (reflux conditions) to obtain the solution. The highest concentration that could be obtained by this method was 1.6 wt. % solids. This narrow range of solubility was limited by the fact that all more highly concentrated mixtures gelled irreversibly upon cooling from the 'solution formation' temperature of 175°C. Chapman and Anolick disclose such findings in their patent examples as well. [7, 8] It appears that an upper limit of solubility was determined at 3 wt. % copolymer content in the perfluorinated solvents in the patent literature. Attempts were made in this laboratory to find better miscibility with the other perfluorinated solvents listed in Figure 1.3, with no success.

Upon repeated attempts at making these solutions in this laboratory, it was observed that a clearing was consistently occurring while heating and stirring to the 175°C solution formation temperature. The various concentrations all cleared at ~50°C. On further investigation of this phenomenon, it was found that mixtures that look and act like solutions at ~50°C could be maintained for concentrations up to 12 wt % solids. This finding opened up a new field of solvent-processing for FEP coatings. The coatings can be made in a single application of the 'solution' for coatings ranging in thickness anywhere from 100nm to 80μm, for the SF-25 copolymer. Details of these procedures are given in the patent application which has been submitted as provided in Appendix 1.

As stated, processable mixtures of SF-25 and PP11 can be formed for all concentrations up to 12 wt % solids. The behavior of the system is mapped out in Figure 2.3, where the shaded area is the range of processability. The lower curve is the clearing temperature observed visually for each of the mixtures at ~50-60°C across all

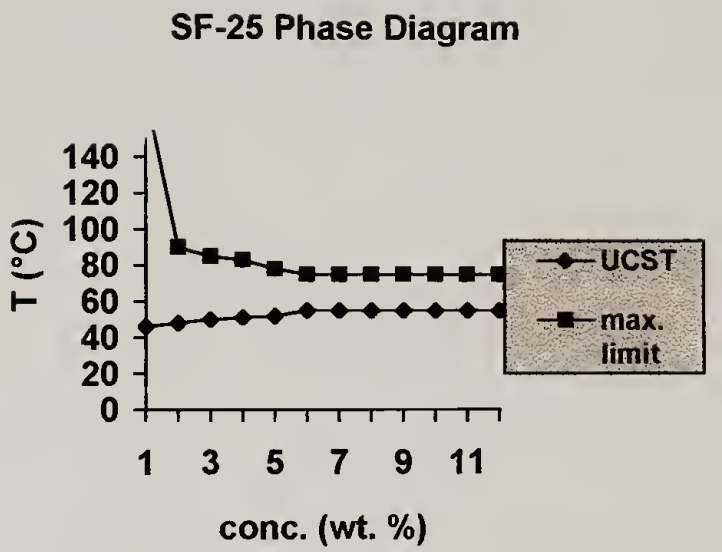


Figure 2.3: Solution behavior of SF-25 in PP11

concentrations. The upper curve corresponds to the temperature limit above which some further interaction is enabled which causes the mixture to irreversibly gel on cooling, as observed earlier. If the temperature is maintained below this critical temperature for the given mixtures, they become more and more viscous on cooling to room temperature, but can be heated back to 50-60°C to achieve the liquid-like properties required for processing. In other words, by not going above the critical temperatures depicted on the upper curve, reversible clearing will occur upon heating and cooling through ~50°C. If, however, the critical temperatures are exceeded, on cooling from the higher temperatures, the mixtures will irreversibly gel as a clear gel. Over time, the mixtures become turbid again. Some gelled mixtures becoming turbid over time were described in the patent examples by Anolick, however the clearing phenomenon was never mentioned or investigated. [8]

Gelation Phenomenon

The gelling transition that occurs is very curious. The system clears at ~50°C as if it is beginning to form a solution. At this temperature and above, the system acts as if it is a solution by exhibiting clarity and increased viscosity over the original turbid dispersion at room temperature. Another important aspect of the behavior is that above the upper temperature limit, bubbles form in the mixture for all concentrations. The temperatures shown for the upper curve are primarily anywhere from 75°C -95°C. This temperature regime is well below the melting and degradation points of the polymer, as well as the boiling point of the solvent (215°C). Finally, upon cooling, any concentration of 2-3 wt % or higher turns to a clear gel. Therefore, there seems to be a concentration

dependence associated with the gelation. Then, as mentioned, over time (several days) the mixture becomes turbid again in a sealed container. Finding a cause for such gelation behavior was investigated to possibly avoid it in continued experimentation.

Solvent Degassing Study

The bubble formation seems coincident with the upper temperature limit. The cause for the behavior is probably due to the solvent having a high affinity for absorbed gas. The typical solubility of gases in perfluorinated solvents is shown in Figure 2.4. By referencing the typical inverse relationship between temperature and gas solubility for perfluorinated solvents (Figure 2.5), it is safe to assume that the bubbles observed are a result of the gases being forced out of solution at elevated temperatures. It was suspected that the absorbed gases may, therefore, be somehow aiding the solubility of the SF-25 in PP11, and when removed, cause the system to crash and gel irreversibly.

Freeze pump thawing is a standard procedure used in a chemistry laboratory to remove unwanted absorbed gases from liquids. It is based on crystallizing the solvent to force the gases out of solution. The solvent is brought below its freezing temperature, the chamber is then evacuated to remove the unwanted gas, and finally the system is closed off under vacuum, and the system is allowed to warm to room temperature. The procedure is repeated until no more gas comes off, evidenced by little to no pressure build up in between evacuations. This technique was applied to the solvent alone and also different concentrations of the SF-25 mixture. Afterward, the mixtures were brought through the temperature profiles used normally in forming the solutions.

TABLE 17

TYPICAL SOLUBILITY OF VARIOUS GASES IN "FLUORINERT" LIQUIDS AND WATER AT 1 ATMOSPHERE & 25° C

GASES	ml. GAS/100 ml. "FLUORINERT" LIQUIDS									
	Water	FC-72	FC-84	FC-77	FC-104	FC-75	FC-40	FC-43	FC-70	FC-71†
HELIUM	.09	11	10	10	9	9	6	6	5	4
ARGON	*5.6	65	59	56	52	55	37	36	31	26
HYDROGEN	1.9	17	15	15	14	14	10	10	8	6
NITROGEN	1.6	43	39	37	34	39	24	24	20	16
OXYGEN	3.2	65	59	56	52	51	37	36	31	26
CARBON DIOXIDE	80.5	248	224	214	199	209	142	140	117	94
AIR	1.9	48	43	41	38	40	27	26	22	18
METHANE	3.3	92	83	80	74	78	53	48	44	40
ETHANE	4.5	282	255	243	227	238	162	159	133	107
TETRAFLUORO-METHANE	**	129	117	111	104	109	74	72	61	50
SULFUR HEXAFLUORIDE	**	957	863	826	769	807	548	540	453	366
CHLORINE		1350	1220	1165	1085	1138	773	753	639	525
AMMONIA		54	48	46	43	45	31	30	25	20.
FLUORINE		17	16	15	14	14	10	10	8	6
KRYPTON		118	106	102	95	100	68	66	56	46

*Measured at 0° C.

**Slightly soluble as reported in Handbook of Chemistry and Physics, 48th edition, edited by Robert C. Weast, published by Chemical Rubber Company, Cleveland, Ohio, 1967.

†35°C.

Figure 2.4: Gas solubility in typical perfluorocarbon solvent

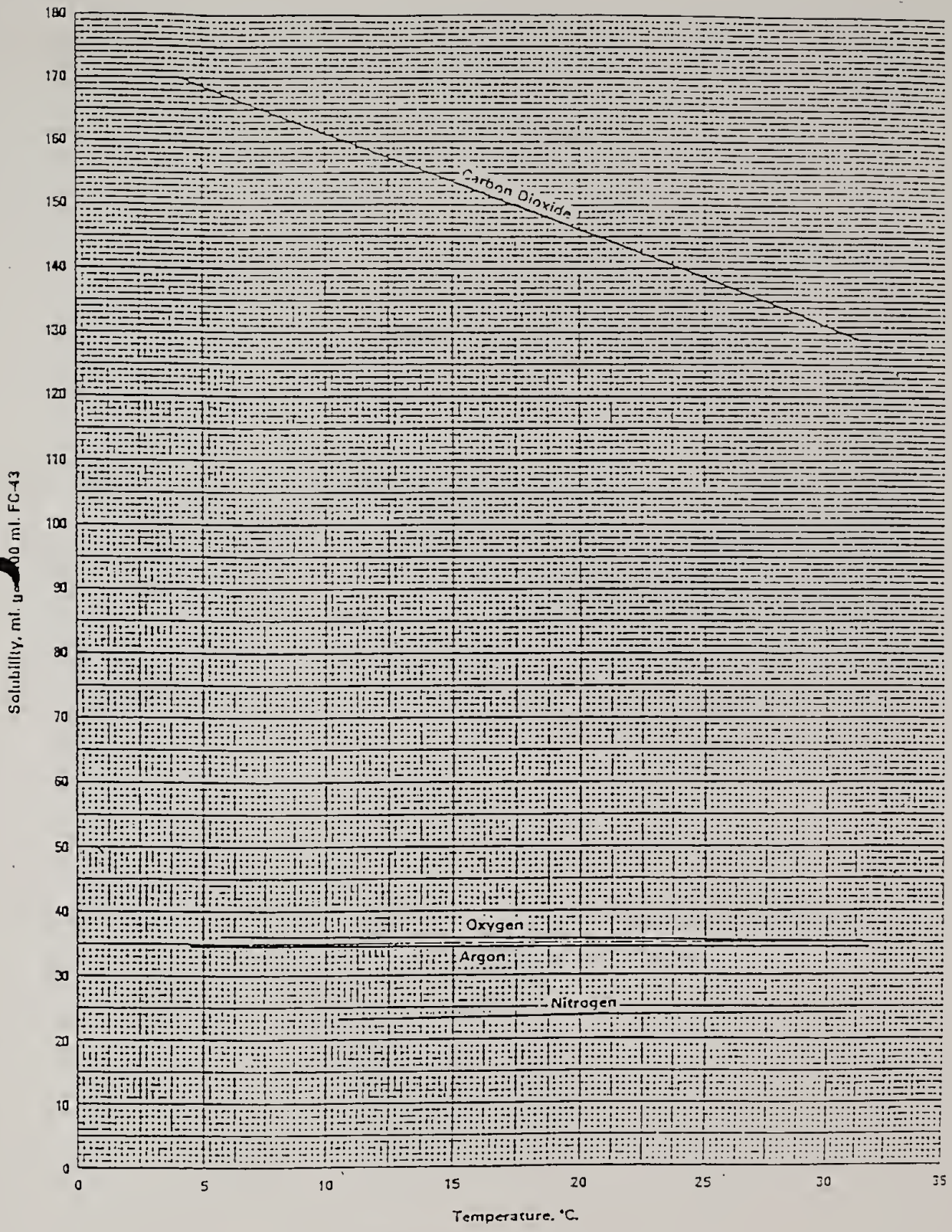


Figure 2.5: Gas solubility dependence on temperature

Comparisons were made between the behaviors of the normal and degassed mixtures. The degassed mixtures exhibited no behavioral differences from the normal mixtures. The gas solubility can therefore be eliminated as a source of gelation.

Entanglement Theory

This then leaves one other possible explanation for the gelation on cooling from the higher temperatures. Some new interaction between polymer-polymer or polymer-solvent must be enabled at the higher temperatures. Based on the unreactive, nonpolar nature of both the solvent and the polymer, a polymer-solvent chemical reaction at such low temperatures is unlikely. Physical interaction between the two is also unlikely since no evidence of the cyclic fluorinated species is apparent in IR or thermogravimetric analysis (TGA) data taken on the films. IR data is shown in Figures 2.6 and 2.7 taken from solution cast and dried films. The cyclic species would show up at higher wavenumbers. Also, TGA of the films shows no weight loss below 325°C as shown in Figures 2.8 and 2.9, and the boiling point of the solvent is 215°C. Therefore, it is believed that a new polymer-polymer interaction is enabled at these higher temperatures.

Again chemical linking is unlikely due to the stability of the polymer at these temperatures. An interaction which best describes the observed characteristics of this mixture is an entanglement theory or physical gelation. De Gennes describes three main possible routes to physical gelation which are apparent in polypeptides, polysaccharides and isotactic polystyrene. [9] There could be a formation of helical structures with two or more strands, a formation of microcrystals in chain segments that are not

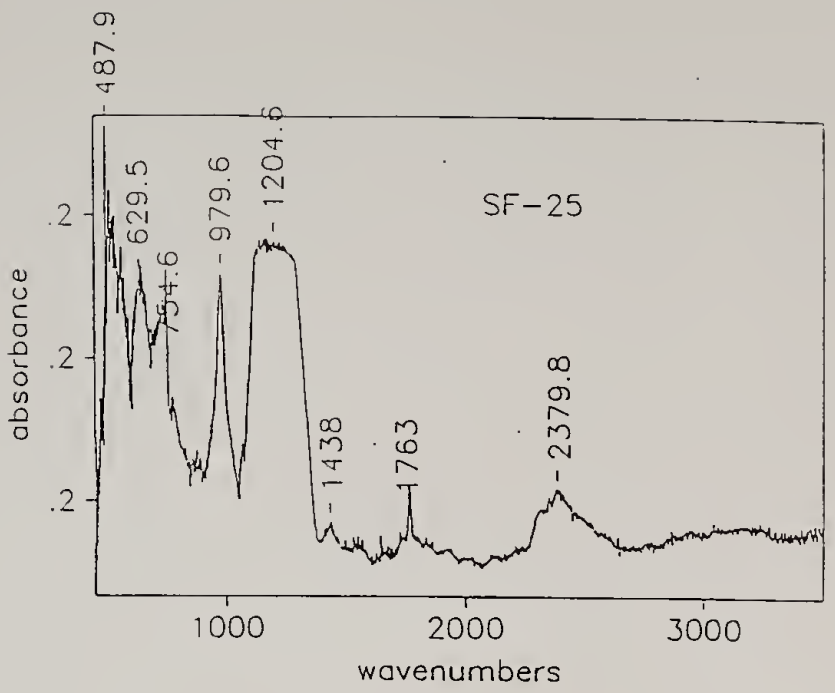


Figure 2.6: Infrared spectra of SF-25

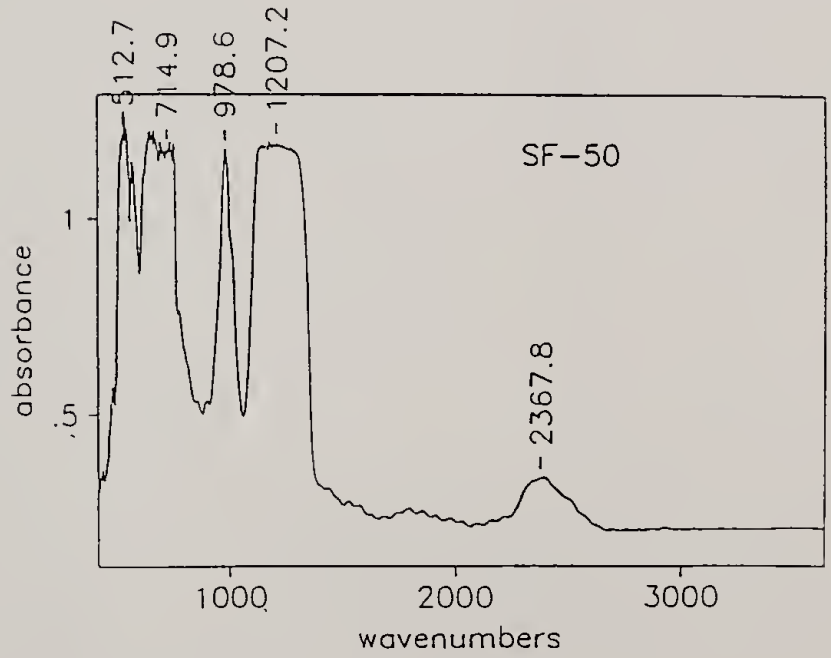


Figure 2.7: Infrared spectra of SF-50

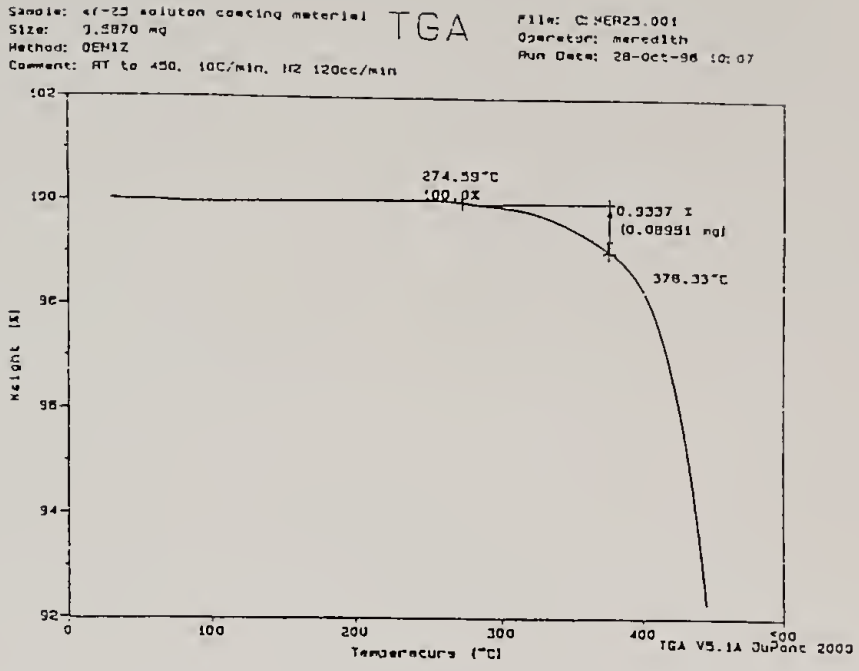


Figure 2.8: TGA analysis of SF-25

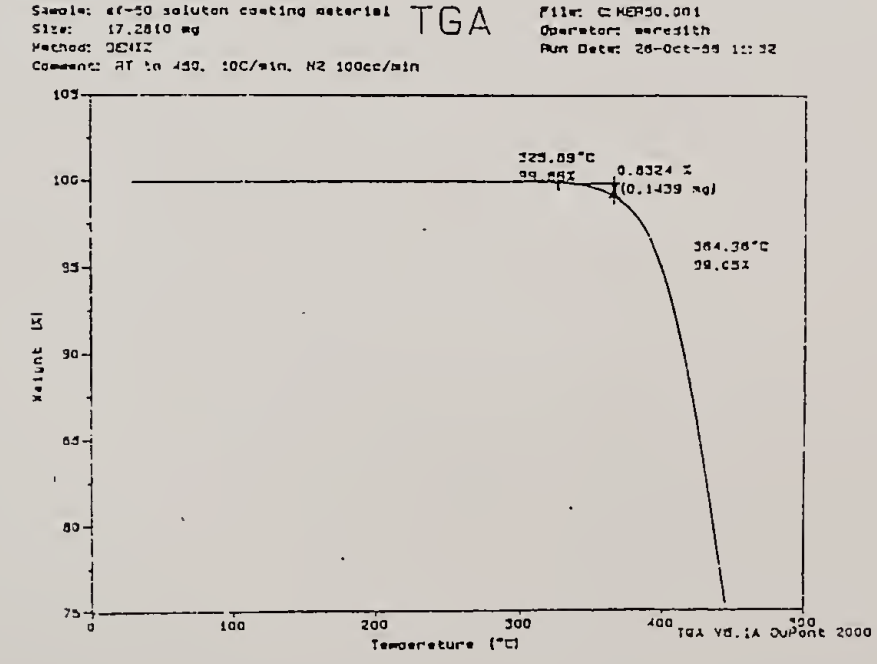


Figure 2.9: TGA analysis of SF-50

stereoregular (so that it cannot pervade the entire material), or nodules formed by association in block copolymer structures. The latter is ruled out here due to the random insertion of the HFP comonomer. Helical structures could be a possibility here since PTFE and FEP are known to conform into a twisted zigzag arrangement (see Chapter 5). Finally, the SF-25 polymer could be irregular in the sense that there could be HFP-rich phases and TFE-rich phases along the backbone. This could enable the microcrystalline regions.

For isotactic polystyrene, IPS, it is believed that the concentrated solutions at low temperatures form secondary crystalline structures in the form of fringed micelles. [10-13]. The cause for such secondary configuration was originally speculated as either areas along the chain that stray from the isotactic regular structure or from a change in the helical twist of the isotactic chain itself. Later, neutron and x-ray scattering results pointed to a change in helical conformation. A new extended chain *tt* (trans, trans) conformation causes the helix to change to a 12_1 helix instead of the normal *tg* (trans, gauche) conformation exhibiting a 3_1 helix in crystalline IPS. [14, 15] At low temperatures for IPS in solution, the chains start aggregating. Due to the irregularity arising from the different helical twist, the chains aggregate into fringed micellar structures instead of the lamellar crystal structures. The arms of the micelles are of the same kind and, for concentrated solutions, they aggregate with arms of neighboring micelles to form microcrystals or helical bundles. This physical interaction throughout the material is what causes the gelation.

In this case of the SF-25, a similar phenomenon seems to be taking place. At room temperature the fine powder particles are merely dispersed in the PP11 and the

mixture is cloudy. As the system is heated, swelling is initiated as the temperature nears the glass transition temperature of ~50°C. This temperature is coincident with the observed clearing point described above. When the solvent diffuses into the polymer particles, the crystal packing is disrupted as evidenced by the visible clearing. At some temperature above this clearing point, the chains probably reorient into a fringed micelle type structure with HFP-rich phases separating from TFE-rich phases. The micelle crystal structure occupies a much larger volume than the hexagonally packed crystals normally observed. As the temperature increases, the micelle volumes grow larger. For more concentrated solutions, the micelles can overlap and either helical bundles or microcrystals can form.

The critical temperature for such entanglement depends on concentration and this relationship is given by the upper curve in Figure 2.3. The critical concentration appears to be the 1.6-3 wt % concentration initially pinpointed by the DuPont researchers. Based on the assumption that most of the 2μm mesh particles are spherical and of the mesh size, roughly 300% volume change must occur for any interaction to take place at 3 wt% polymer in solution. This swelling requirement decreases for more concentrated systems and is reflected in the lower temperatures observed for their upper critical points.

To further justify these claims, an experiment was done to determine if actual dissolution occurs at the 50°C clearing temperature. An SF-25 film, which had been cast and dried from the solvent processing at ~50°C (method described in Chapter 3), was then cut into small pieces (1 cm^2) and submerged in the PP11. The solvent cast film has the same crystalline structure as the as received powder, which is evidenced by x-ray

diffraction in Chapter 5. The same procedure of low temperature mixing was performed and the film pieces all swelled visibly to larger squares (1.5-2 cm^2), but never dissolved. To corroborate the entanglement theory, the pieces were then taken to 120-130°C and cooled. As mentioned, when the powder was mixed and taken to this temperature it gelled irreversibly on cooling. For the film pieces, no gelation (linking between pieces) occurred on cooling since the pieces did not have intimate mixing like that of the powder particles.

Light Scattering

Dynamic light scattering was employed at an early stage of this investigation to try and pinpoint the gelation phenomenon on cooling. Dilute solutions (1-3 wt%) were prepared and loaded into the apparatus equilibrated at 50°C. The solutions were exhibiting abnormal scattering from very large particles and dust was visible in the vial. The solvent was first filtered and then the solutions were made and still dust was visible (obviously from the polymer powder). Therefore the solutions were made and then filtered, and again loaded in the light scattering apparatus.

The results showed no evidence of any polymer in the 1 and 2 wt % solutions. The filtering step had removed all of the polymer. The filter used was a 0.22 μm pore size PTFE filter. This experiment also shows that there is incomplete dissolution of the SF-25 in PP11 at these lower temperatures and that the particles present are very large.

SF-50

The SF-50 copolymer with the 50:50 mole ratio of HFP:TFE is soluble in the solvents given in Figure 1.3. The mixtures can be left overnight at room temperature

and the polymer will go into solution by itself, or the mixture can be heated and stirred to obtain solubility in a shorter time period (~ ½ hour). No upper critical solution temperature (USCT) is observed above room temperature. Once the polymer goes into solution it remains as such at ambient temperatures. Table 2.1 lists the solvent system with SF-50 and the maximum concentration achievable before the solution is too viscous to pour.

Table 2.1: SF-50 solutions

Solvent	Max wt. % solids
PP11	9
FC-40	10
HFB	10

Summary

SF-25 contains 25 mole % HFP and exhibits partial miscibility in PP11, a high boiling perfluorinated solvent at ambient pressures and moderate temperatures. While not becoming fully dissolved, the swollen dispersion of the polymer in the solvent makes a very useful new medium to process coatings of FEP on various substrates. SF-50 contains 50 mole % HFP and exhibits full miscibility in PP11, FC-40, and HFB solvents. Both systems can be used for standard coating methods to achieve thin TFE:HFP copolymer coatings.

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CHAPTER 3

MAKING SOLUTION-CAST COATINGS

Introduction

The new fluoropolymer swollen dispersions and solutions described in Chapter 2 can be processed by standard coating techniques. Several different approaches are available to solution-cast a film onto a substrate and, in this investigation, each option has been explored. Spin coating inherently produces thin films from solution, which will be in-plane isotropic, due to the nature of the process. However, the thickness can be controlled by varying the RPM of the stage and the solution concentration. Slower speeds and higher concentrations should lead to thicker films. For dip-coating techniques, however, a slower withdrawal speed results in thinner films. Also, some anisotropy and thickness variation can occur in the draw direction. Finally, blade drawing will be utilized to obtain thicker coatings. A Gardner® doctor blade can be used, of specific height (2-50 mils), to draw a film of the solution across a substrate. Again, anisotropy could result from alignment in the draw direction.

Experimental

Substrate cleaning

A variety of substrates are used here for the coating studies. The investigation has been limited to high temperature materials which can withstand the heat treatment after solution coating. Table 3.1 shows the techniques used.

Table 3.1: Substrate cleaning

Glass	1. wipe down with acetone and Kimwipe
Aluminum	1. etch surface with 20M NaOH solution in H_2O - dab Kimwipe with NaOH, apply to Al surface and let stand for 1 minute, rinse with H_2-O- & dry 2. wipe down with acetone and Kimwipe
Steel, Copper	1. wipe down with acetone and Kimwipe

Spin coating

Spin coating was done at ~550 rpm using solutions of varying concentrations. Dispersions of SF-25 in PP11 @ 50°C, and solutions of SF-50 in PP11 or FC-40 and AF1601 in FC-40 or FC-75 were spun onto glass, aluminum, copper, and steel.

Dip coating

The same sampling of substrate material was dipped into the solutions described in spin coating. The substrate was clamped into the upper grip of an Instron® 8511 hydraulic control tensile tester. The withdrawal speed was computer controlled via the crosshead speed setting.

Blade coating

In order to achieve films of a greater thickness, the solutions were drawn down onto the substrate with a doctor blade made by Gardner®. All the solutions were used at 8 wt % concentration or higher for blade drawing. Since the intent was to maximize the thickness of the film, the largest blade sizes (30 or 50 mils) were used.

Heat Treatment and Solvent Evaporation

The films deposited onto the substrates by the various techniques all had to be heated to evaporate the solvent utilized. Table 3.2 lists the solvents and their respective boiling points.

Table 3.2: Boiling Points of Solvents

	B_p (°C)
PP11	215
FC-40	155
FC-75	140

The heating profiles used were taken to a maximum temperature consistent with the solvent boiling point.

Initially, thin films were being made by spin- or dip-coating and the samples could be placed in a vacuum oven at ~200°C for 2-3 hrs. to evaporate the solvent. In fact this was desired especially for the very thin SF-25 films on Cu, since the copper would tarnish in a regular convection oven.

Later, however, as thicker films were achieved, it was found that the vacuum evaporated the solvents too quickly and bubbles were unavoidable in the final coating. In fact, placing the thickly coated samples in a preheated 200°C oven with no vacuum caused bubbling problems. Therefore, experiments were done to find the optimum drying conditions for the different materials. The following procedure is representative for all solutions, but is specifically written for SF-25 in PP11. Applying this method to other solvent systems, the last temperature ramp can be skipped.

Table 3.3: Drying procedure

Ramp (°C/min.)	final temp. (°C)	hold time (hrs.)
0.1-5	50	0.5-1
0.1-5	100	0.5-1
0.1-5	150	0.5-1
0.1-5	220	1-2

Allow sample to slowly cool back to room temperature

Contact Angle Measurements

Using Young's theory of surface tension balance, the angle which a liquid surface makes with a solid can be used to characterize the interface and the surfaces involved. [1] The measurement can be used to identify a solid surface, or using Young's surface energy balance, the solid's surface tension can be calculated. For the purposes of this investigation, the contact angle that water makes with the coating material was used to verify the fluoropolymer surface coverage.

Thickness Measurements

A few different techniques have been implemented to measure the thickness dimension of the coatings. Zygo phase interference microscopy and ellipsometry have been used for the thin film measurements (10nm-1μm). [2] [3] For the thicker films, a Mitutoyo digital thickness gauge was used which measures the gap a film produces when contacted by a small flat platen.

Phase interference microscopy is a non-contact laser probe of a surface. Not only does it profile surface roughness, but it also can give thickness variation up to a quarter wave of the laser source wavelength. For the Helium-Neon laser source used, this corresponds to 158 nm.

Ellipsometry is also a non-contact laser reflection technique available for thickness measurements in multiple layer systems.[4] A monochromatic polarized beam of light is projected onto the interface (coating/substrate in this case) in question. The reflected beam has an altered polarization after interfering with the coating material. If the indices of refraction are known for the coating and substrate, the thickness of the coating can be calculated based on the ellipsometric components of the reflected beam. The maximum thickness measurement achieved here is equivalent to the wavelength of the light source.

Results & Discussion

Contact angle measurements shown in Table 3.4 corroborate the fact that fluoropolymer coatings have been accomplished. The values are listed with the literature value for FEP to show consistency. [5]

Table 3.4: Contact Angle with water

Material	advancing	receding
aluminum	65°	18°
SF-25	107-109°	90°
SF-50	107-109°	90°
AF 1601	107-109°	90°
FEP	108°	90°

Initial coating work was done only with SF-25 by spin coating using very low concentrations. After the solution processing technique was discovered, more concentrated solutions enabled coating by using a doctor blade. Some examples from this work are represented in the graph in Figure 3.1. SF-50 solution coating behavior follows the same trends.

Figure 3.2 encompasses some thin film coating work done with AF 1601 in FC-75, another Fluorinert® solvent available from 3M (B_p given in Table 3.2). Dip coating was used to obtain these coatings on PMMA and glass for potential antireflective applications. Teflon® AF has the lowest refractive index, n, for a polymer at 1.31, which makes it the best material for this purpose. To be antireflective, the coating thickness must be on the order of $\lambda/4n$, based on the wavelength of the light to be reflected, λ, and the refractive index of the film. In the visible light range this corresponds to 100-150 nm film thickness for AF 1601, which is easily accomplished by the dip coating process using the given concentrations.

Later work with more concentrated solutions of AF 1601 in FC-40 resulted in coatings up to 100 μm thick. This maximum thickness was accomplished by blade coating 50 mils of 15 wt % solution onto glass, aluminum, or PMMA. Other 50-70 μm thick films have been made either with lower concentrations or thinner solution casts, as with the SF-25 and SF-50.

Table 3.5 shows the ranges of thickness achieved for each of the above procedures. Also the last column provides the thickness measurement device used in obtaining these values. These values are ranges that encompass the data for all three polymers investigated.

Conclusion

Solution coating processes investigated here enable the formation of fluoropolymer coatings requiring very little surface preparation. After discovering new techniques to form more highly concentrated systems, a wide range of coating thickness

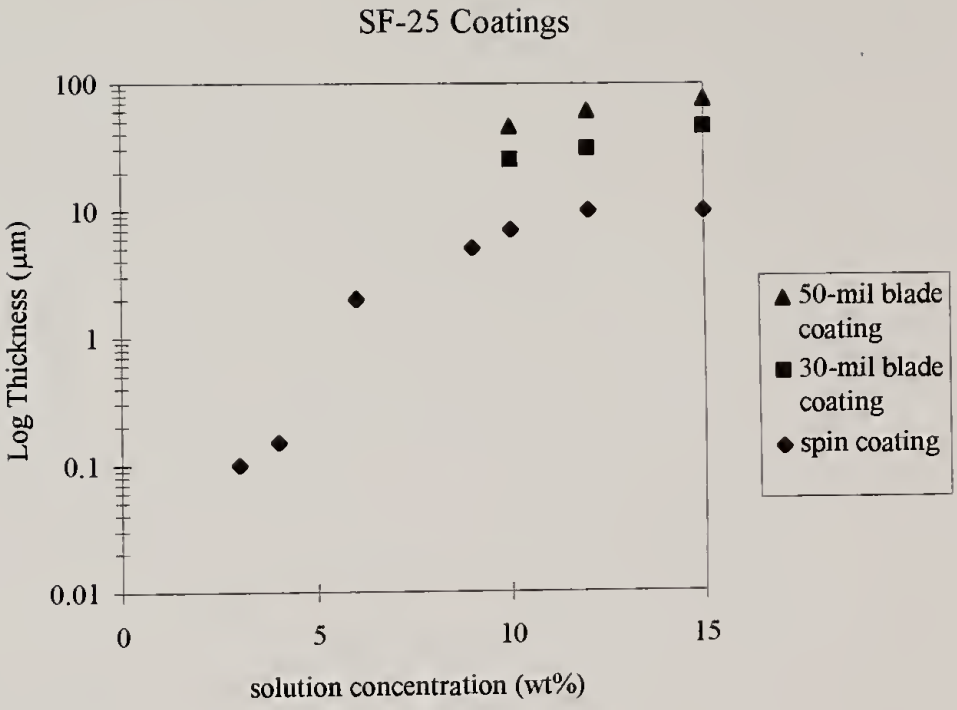

Figure 3.1: SF-25 coating thickness as a function of method and solution conc.

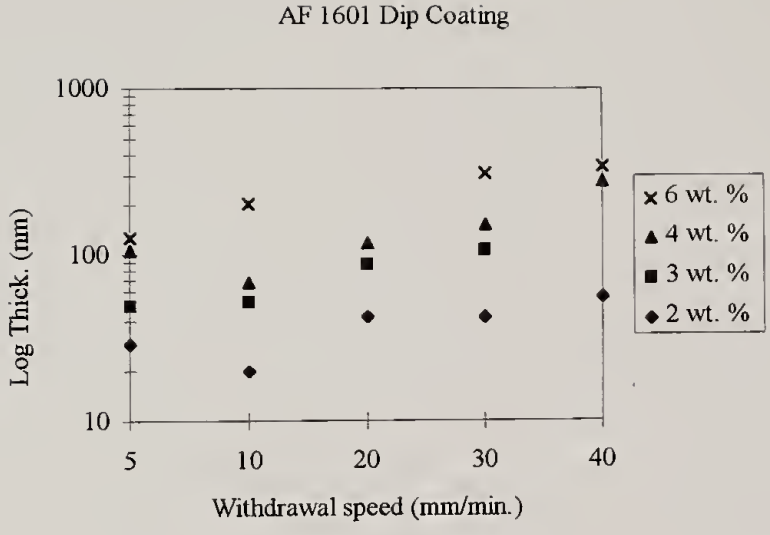

Figure 3.2: AF 1601 dip coating results

Table 3.5: Coating Results

Coating Procedure	Solution Conc. (wt%)	Thickness range (μm)	Meas. Device
dip coating	3-6	0.01-1	Ellipsometry
spin coating	3-15	2-10	Mitutoyo gage
blade drawing	3-15	5-80	Mitutoyo gage

was achieved using single coating applications. The thickness level can be as low as required for antireflective properties (50-150 nm), or be much thicker where fluoropolymer barrier properties can be exploited (up to 100 μm). Adhesion quality and barrier properties measured are presented in Chapter 5.

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CHAPTER 4

MATERIAL PROPERTIES

Introduction

The materials under investigation here are experimental materials. After determining the solubility, DuPont researchers had not conducted any characterization of physical properties. As a result, experiments have been conducted in this lab to understand processing and performance windows.

Mechanical Properties

In terms of coatings, a few mechanical properties are of interest to understand stress states of the coating film in use. The Young's modulus provides insight into the stiffness, while tensile strength measurements outline the ultimate stress limits. The modulus value is also important because it is needed in calculating the coating's strain energy which plays a key role in its adhesive behavior, which will be described in more detail in Chapter 6. The in-plane stresses also effect the coating performance. Holographic interferometry is used to measure this stress state. By knowing the stress values, combined with the material's ultimate strength, the coating performance can be better predicted. Dynamic mechanical testing monitored at fixed frequency over a temperature range is also an important method used here to understand the mechanical behavior of the coating at elevated temperatures and reveal any transitions that occur in the temperature range of interest.

Tensile testing

An Instron® 5564 has been used in tensile mode to measure the modulus, breaking strain, tensile strength and yield strength of the fluoropolymers being investigated. ASTM Standard D882 was followed on solution processed films of SF-25, SF-50, and AF1601. All the films were prepared as described in Chapter 3, using concentrated solutions to obtain films ~70 μm thick. The films were then cut to ASTM standards in a 8:1 length to width ratio and mounted between manila paper using Super glue® at the ends to provide enhanced gripping in the pneumatic grips. Tensile tests were performed at 10%strain/min. (crosshead speed = 4mm/min).

In-Plane Stresses

For coating materials, the stresses acting in the plane of the film are critical to its end-use performance. Problems such as delamination, cracking and buckling can occur in a coating depending on the types of stresses acting across it: anisotropic or isotropic, tensile or compressive. Holographic Interferometry is a technique used in this laboratory which can be used to determine these stresses.[1] It is based on the fact that a membrane under isotropic conditions, will vibrate in response to shaking. At certain characteristic frequencies, the membrane will resonate and form unique mode shapes. By identifying these mode shapes and taking the density of the membrane and its geometry into account, the biaxial stress can be calculated.

The theory behind this technique is based on the vibration of a membrane which has a behavior described by the following equation,

$$\sigma \nabla^2 u = \rho \frac{\partial^2 u}{\partial t^2} \qquad (1)$$

where σ is the stress in the membrane, u is the out of plane displacement, and ρ is the density. By solving this differential equation and applying the boundary condition of no displacement at the outer edges of a circular membrane of radius, R, the stress in the film can be written as:

$$\sigma = 4\rho\pi^2 R^2 \left(\frac{\nu_{mn}}{Z_{mn}}\right)^2 \qquad (2)$$

where Z_{mn} is the n^{th} zero of the m^{th} order Bessel function. As one can see, the only material property that is required is the density. Otherwise, the resonant frequency, ν_{mn}, is measured for a given mode of vibration, corresponding to Z_{mn}.

For this particular experiment, the samples will be prepared by, first, solution coating a substrate, such as aluminum, with the FEP. Then, a rigid steel ring can be affixed to the surface of the coating or to the aluminum substrate. Finally, the aluminum substrate will be etched away using an NaOH solution, leaving the coating film mounted as a membrane on the steel ring. This procedure will effectively trap in the residual coating stresses in the FEP, since no stresses are transmitted at the coating-substrate interface except within a few thickness' of the free edges.[2]

SF-25 and SF-50 Sample Preparation

Under normal circumstances, a steel washer would be affixed to the top of the coating material using an adhesive like epoxy. However, due to the non-wetting nature

of the FEP surface, a new approach was required to mount the FEP film on the washer. Care must be taken to trap the stresses in the film as it is a coating on the given substrate. For these experiments, aluminum shim (~125 μm) was used for the substrate which could subsequently be etched away. To overcome the adhesion problems between the washer and the coating, the washer was affixed to the underside of the aluminum as shown in Figure 4.1. Epon 828 mixed with a curing agent was used as the adhesive. The inner circle of the aluminum was then etched with aqueous 10M NaOH.

Teflon AF 1601 Sample Preparation

For the AF polymer, there was somewhat of a different problem to overcome. It also had the difficulty of adhering something to the coating surface, but it had yet a greater problem to overcome. The coating would spontaneously pop off the substrate with very little agitation. It would not survive the underside washer mount and subsequent aluminum etch like the SF polymers. Therefore, the film was mechanically attached to the washer, as shown in Figure 4.2.

Here, two washers were used that could be clamped together by screwing one to the other with three screws. The AF 1601 was blade coated onto the aluminum shim from a 15 wt. % solution of the AF in FC-40. After heating to remove the solvent, the coated aluminum was sandwiched between the two washers. The three holes were poked through the sample using an Exacto knife, and then the sample was clamped into place with the screws. Finally, the exposed inner circle of the aluminum was etched away with the aqueous 10M NaOH.

Steel washer

cross-section of mounted washer
under coated Al sample

Figure 4.1: SF-25 and SF-50 holography sample prep.

Figure 4.2: AF 1601 holography sample preparation

Density Measurement

Since density is the only material quantity required for the stress calculation described above, it is measured here for accuracy. The literature values for density of FEP and AF are 2.13-2.15 and 1.78 g/cm^3, respectively. [3, 4] A buoyancy technique can be used for this procedure which is based on a dilatometric study done by Kolb and Izard. [5] The sample film is freely hung on a hook which is attached to the underside of an analytical balance. The weight, w, is measured for the sample in air and then again after the sample is completely submerged in a fluid of lower density, so that the sample sinks. Here, silicone oil is used which has a density of 0.963 g/cm^3. The sample density can be calculated according to the following relations:

$$\rho_{sample} = \frac{w_{air}}{V_{sample}} \qquad \text{where,} \quad V_{sample} = (w_{air} - w_{oil}) \div \rho_{oil}$$

The weight of the wire is subtracted out where necessary.

Dynamic Mechanical Properties

The modulus that was measured, as described in the Tensile testing section of this chapter, is not invariant. As with all polymeric materials, these fluoropolymers will exhibit a temperature dependent modulus which can be measured through dynamic mechanical experiments. [6] In a dynamic test, the sample is subjected to a sinusoidal strain history. If the strain is described by the function $\varepsilon(t) = \varepsilon_o \sin\omega t$, then the stress response will be $\sigma(t) = [E'(\omega)\sin\omega t + E''(\omega)\cos\omega t]\varepsilon_o$. For a perfectly elastic material, the modulus, E', is a constant and E'' = 0, therefore the stress response is in-phase with

the imposed strain function. However, if the material is viscoelastic, the stress will lag the strain by some amount. The result is a frequency dependent modulus that can be broken up into in-phase and out-of-phase components, or real and imaginary components, E' and E". The ratio of these two components, E"/E', is tan δ, or the loss tangent. E' is generally referred to as the storage modulus and E", the loss modulus. An example of a typical temperature profile of the storage modulus is given in Figure 4.4. This curve is an example of the behavior of Teflon® FEP 100 and can be used as a control in the data collected here. All three values discussed above, E', E", and tan δ, are usually output from a dynamic test and can reveal information about the material behavior.

A Rheometrics Scientific Instruments Dynamic Mechanical Thermal Analyzer (DMTA) Mark IV was used in tensile mode on the thin solution-processed films prepared as in Chapter 3. The parameters were matched to the specimen toughness by performing a test designed to pinpoint the proper strain amplitude and force applied. All tests were done at 1 Hz frequency in a temperature range that would center around the T_g of the sample.

Results & Discussion

Figure 4.3 shows the results taken from the tensile tests including literature values of Teflon® FEP for comparison. The data provided shows that the solution processed FEP's have modulus values which are the same or better than those given for FEP 100. Table 4.1 lists the results of the flotation technique, ρ, as well as the isotropic coating stress, σ, for each sample calculated from frequency measurements taken for the

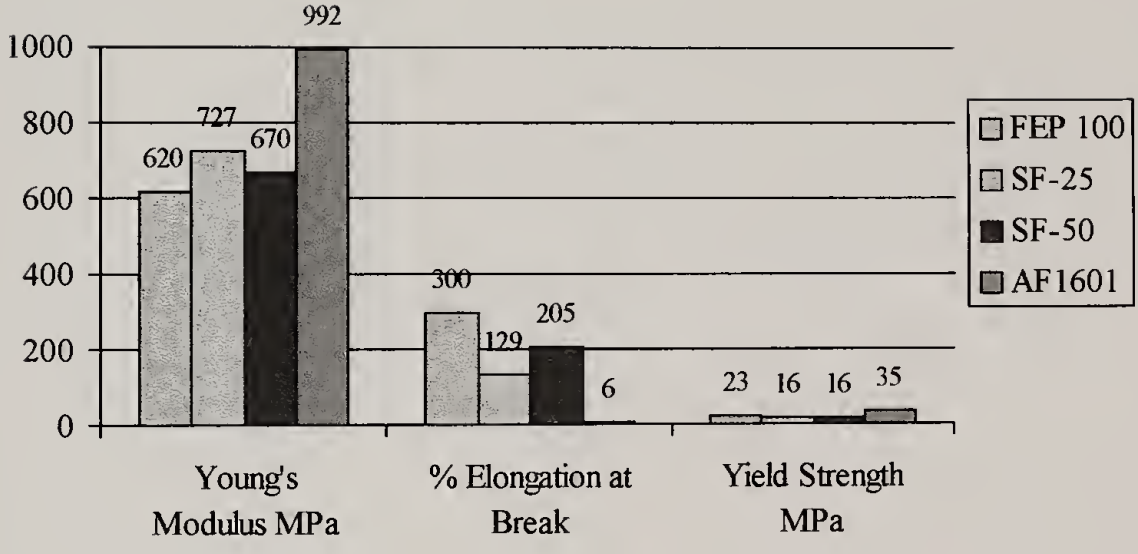

Figure 4.3: Mechanical properties from tensile testing

first several zeroes of the Bessel function or modes of vibration. The stress was calculated using equation 4.2. Both the SF-25 and SF-50 have very low stresses in the film resulting from the coating procedure used. AF1601, on the other hand, is very highly stressed when coated on either glass or aluminum. This can be reflected in the fact that AF 1601 easily pops of the substrate

Table 4.1: Densities and In-plane stresses

Sample	ρ (g/cm^3)	σ (MPa)
SF-25	2.18	2.2
SF-50	2.03	0.0
AF 1601	1.81	31.5

and, in contrast, the SF polymers do not show any delamination. Such behavior will be described in more detail in the next chapter.

Figures 4.4-4.7 show the results of the DMTA tests for SF-25, SF-50, and AF 1601, respectively. The starting E' values for each curve corroborates the tensile testing modulus values given in Figure 4.1. However, the modulus drops off quite dramatically in all three cases at the glass transition temperature. The FEP copolymers have transitions at relatively low temperatures which must be taken into account when choosing its usage potential. Also, the tan δ curve peaks at the glass transition temperature of the material, which will be investigated further in the next section.

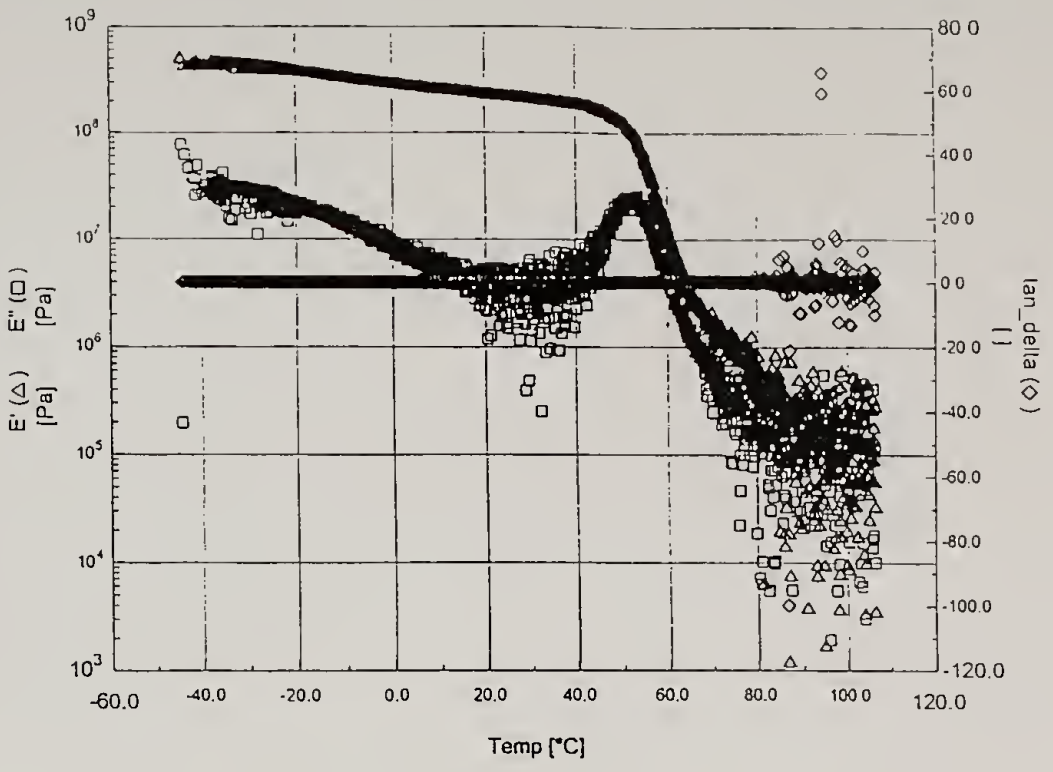

Figure 4.4: DMTA results for SF-25

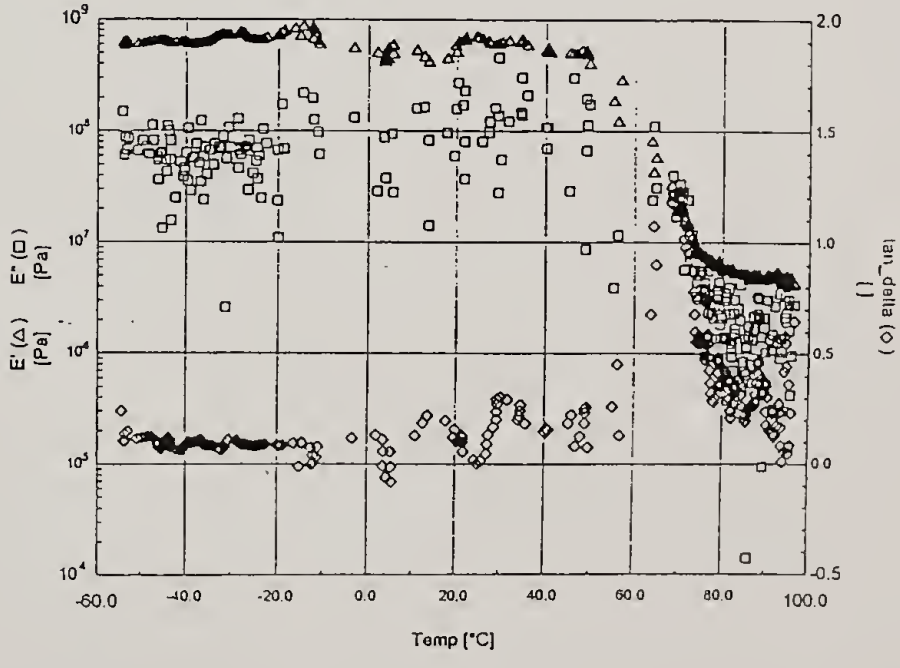

Figure 4.5: DMTA results for SF-50

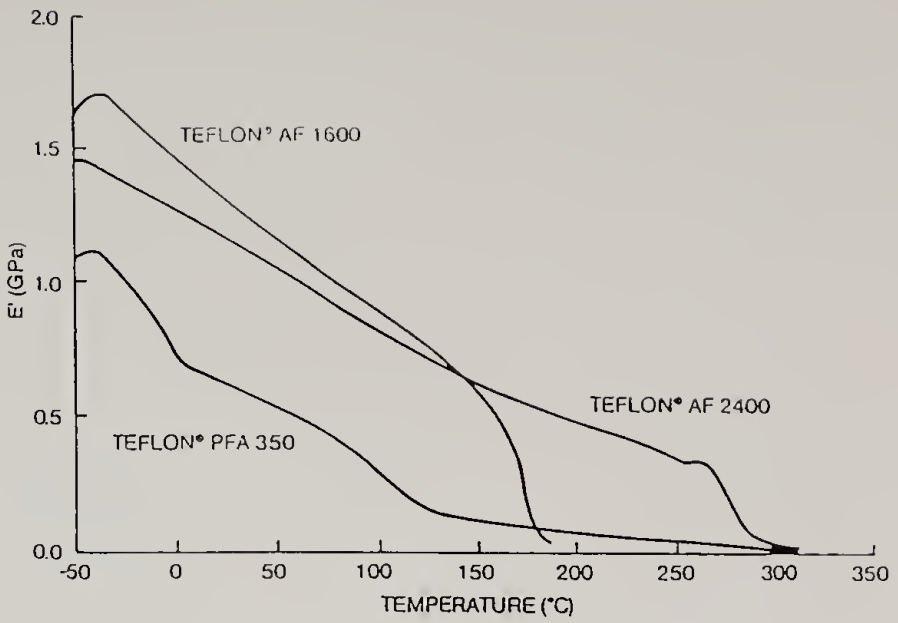

Figure 4.6: Storage modulus (E') vs. temp. for Teflon® AF materials [4]

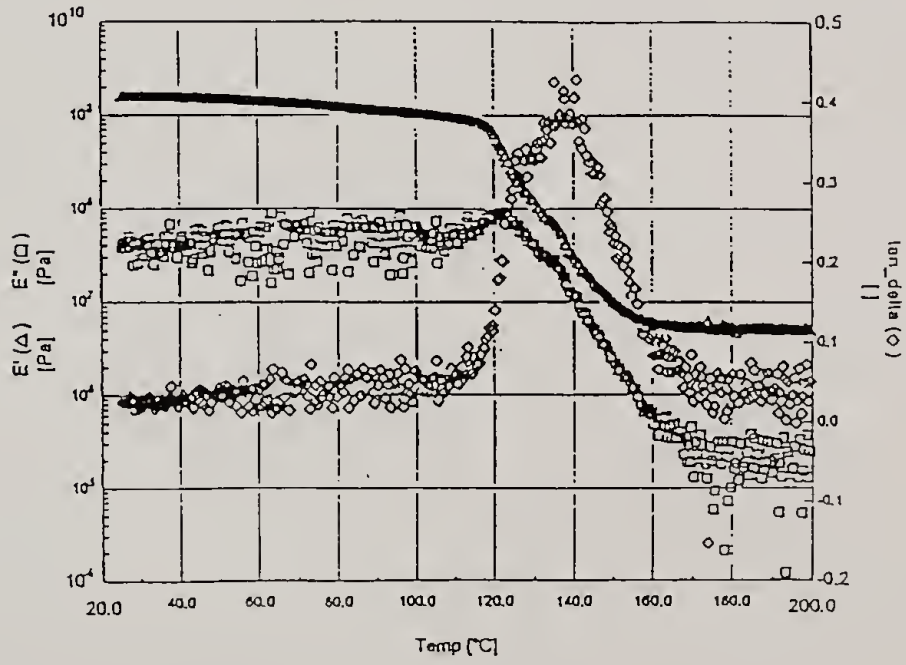

Figure 4.7: DMTA results for Teflon® AF 1601

Thermal Properties

Thermal properties are of tremendous importance when deciding on an optimum coating. Polymeric materials, especially, have thermal transitions that change the materials' physical properties to a large degree. For instance, the glass transition temperature (Tg) is a softening point that coincides with a drop in modulus of about three orders of magnitude (shown above) and an increase in the rate of thermal expansion. Any semicrystalline polymer will have a T_g due to the amorphous regions present. Differential scanning calorimetry (DSC) is used along with thermal gravimetric analysis (TGA) to pinpoint the glass transition temperature, the melting point, and the onset of thermal degradation by measurement of weight loss with temperature.

The melting transition is a first order transition which corresponds ideally to a discontinuity in the differential of Gibbs free energy, or volume. In other words, the volume expands quickly at the melting point of the crystals. This corresponds to a peak in the second differential of Gibbs free energy or the heat capacity of the material with respect to temperature. The glass transition temperature, on the other hand, is a second order transition and corresponds ideally to a discontinuity in the second differential of free energy or slope of heat capacity versus temperature. A typical DSC thermogram plots the heat capacity vs. temperature and will reveal both of these transitions.

Experimental

A TA Instruments® DSC 2910 is used in this study on samples in the form of the as-received powder and the solution-processed films at 5°C/min. heating rate. A thermal

mechanical analyzer (TMA) is used to measure the linear coefficient of thermal expansion (CTE) of a material, α. Again, a TA Instruments® 2940 TMA is used on solution processed films with the film/fiber attachment at 5°C/min.. Finally, a TA Instruments® 2920 TGA is used on the powder and film samples at 10°C/min.. All thermal analysis experiments were performed in a nitrogen atmosphere.

To corroborate the melting transitions in the fluoropolymers, temperature controlled birefringence studies were done to observe the crystals melting. An Olympus microscope equipped with a hot stage was ramped in temperature at 3°C/min. from room temperature through the temperature where the sample lost its birefringence. Also, simple melting point apparatus (M.P.A.) measurements were done where the melting temperature was taken as the onset of flow in the particle.

Results & Discussion

Table 4.2 shows the results of all the thermal analysis described above. The PTFE data and the FEP 100 CTE data are taken from literature. [7] A few things to note are the consistent decreases in the T_g, T_m, and ΔH as the HFP content increases. This would correspond to less tightly packed crystals and lower overall percent crystallinity with increased HFP content. For SF-50, the melting transition is not observed by DSC in either a regular or modulated DSC mode. The melting point apparatus (M.P.A.) does show a transition around 150-160°C, however. All melting transitions were further corroborated by the optical birefringence tests. The CTE values remain relatively unchanged with changing comonomer content.

Table 4.2: Thermal Analysis Results

Sample	T_g (°C)		T_m (°C)		ΔH (J/g)	CTE(μm/m°C)
	DSC	TMA	DSC	M.P.A.	DSC	TMA
PTFE	120		327			100
FEP 100	80-90		261	260-270	24	135
SF-25	50	49	175	185-195	2-3	130
SF-50	30	30	-	150-160	-	130

Based on this thermal analysis, the powder samples behaved no differently than the solution cast films. The films are transparent but show thermal evidence of partial crystallinity which is further corroborated in the next chapter by x-ray diffraction analysis. Due to the difficulty in detecting melting transition information by DSC for SF-50, the heat's of melting for the copolymers are not compared here to determine the degree of crystallinity. The exact cause for the difficulty in this detection is unknown at this point. The degree of crystallinity is determined by x-ray methods instead.

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CHAPTER 5

EFFECT OF COPOLYMER CONTENT ON CRYSTALLINITY

Introduction

As described earlier, the intent of the FEP copolymer design was to decrease the PTFE crystallinity and melting transition temperature to enable simpler processing. It has been documented in the literature that the crystallinity does in fact decrease from 95-98% for PTFE to ~70% for FEP 100. No work has been done however to elucidate the crystalline changes for the incorporation of up to 50 mole percent HFP now exhibited in SF-50. It is to be expected that the increased solubility achieved in SF-25 and SF-50 is related to changes in crystallinity and crystal structures compared to the commercial grades.

Review of Previous Literature

The homopolymer, PTFE, is 95-98% crystalline with the chains possessing a helical twist which pack into a hexagonal lattice structure. This structure is well characterized in previous literature [1-4], but will be reviewed here as the polymer serves as a control in the experiments performed. The helix takes on different configurations depending upon the temperature range. Below 19°C, the PTFE twists into a 13/6 helix with a nearest neighbor lattice spacing of 5.62 Å. However, above 19°C, the helix relaxes into a 15/7 helix, and the lattice spacing enlarges to 5.66 Å to accommodate the relaxation. Since all measurements in this study were performed at ambient temperatures (~25°C), the latter configuration is the relevant control structure.

It has been shown that incorporation of a second monomer in the TFE synthesis reduces the crystallinity and also changes the crystal structure.[5, 6] By using HFP as the comonomer, which does not homopolymerize under the same conditions, the copolymer structure is believed to be random. [6, 7] At a loading level of 13 % HFP in Teflon® FEP 100, the crystallinity is reduced from ~95% in PTFE to 70%. It is reasonable to assume that the increased amorphous content is probably a result of a higher HFP content along the chain such that the crystalline regions cannot accommodate these larger units without difficulty.

In this chapter, FEP's with varying HFP content were studied with regard to both the effect on crystal structure and degree of crystallinity. This provides the most extensive study of morphological dependence of FEP on the copolymer composition to date.

Experimental Section

Materials

The samples used in the following study consisted of the powder (as received) , 1mm thick melt-pressed films, and multiple layers of 50 μm thick solution-cast films where applicable. A Carver Press was used to melt-press the FEP100, SF-25, and SF-50, at 290°C, 200°C, and 190°C, respectively. Solution-cast films of SF-25 and SF-50 were prepared by blade-coating the solutions onto an aluminum substrate with a Gardner blade. The aluminum was then slowly etched away with a 10 M NaOH solution to obtain free standing films.

Wide Angle X-ray Diffraction (WAXD)

Two techniques were employed to fully characterize the FEP copolymers' crystalline structure. First, an initial diffractometry study was performed using a Siemens D500 camera with a Ni-filtered Cu Kα radiation source. The data was collected in transmission mode. Unoriented samples in the form of both powder and melt-pressed or solution cast films (described in the materials section above) were used for each polymer to determine if any differences arose from processing history. No such differences were seen.

A more detailed analysis by WAXD using photographic film on oriented samples. These were obtained by pulling fibers by hand from the melt or (in the case of the PTFE homopolymer) solid state drawing. Here, a Statton camera with a Ni-filtered Cu Kα radiation source was used with a flat plate in an evacuated chamber.

Image Analysis

The Rhinolyzer® image analysis program which was developed for use with x-ray diffraction graphs and photographic patterns was used to analyze the WAXD data. It was used with the unoriented sample results to calculate the degree of crystallinity in each sample tested. Also, the analysis program was implemented to calculate crystal lattice spacings from the photographic patterns obtained from the oriented samples.

Results & Discussion

Unoriented X-ray Diffractometry

Figure 5.1a shows the D500 diffractometer scan for the PTFE homopolymer. The most intense peak occurs at 2θ of 18.1°, corresponding to a inter-planar spacing of 0.490 nm. For PTFE this is the 100 plane (in Miller-Bravais notation). Two other higher angle peaks are evident on the Intensity vs. 2θ plot in Fig. 2, at 2θ = 31.6° and 37.2°. These correspond to the 110 and 200 planes, respectively, with d_{110} = 0.283 nm and d_{200} = 0.244 nm. The hexagonal unit cell dimension, a, can be calculated from these d-spacings and was found to be 0.566 nm for this sample. This value is consistent with the findings of previous researchers. [8].

Figures 5.1 b-d show the results of the diffractometry for FEP 100, SF-25, and SF-50. When compared to the homopolymer, the following trends are observed:

i) the peak occurring at 2θ ~18^0, (100) for PTFE, is shifted to lower angles with increasing HFP content.

ii) the resolution of the higher angle peaks becomes poorer with increasing HFP content.

iii) the half width of the peaks become larger and larger with HFP content.

Table 5.1 depicts the quantitative changes observed in the spectra and the corresponding hexagonal lattice spacing changes. As one can observe, the unit cell enlarges from a = 0.566 nm for the homopolymer to a = 0.647 nm for SF-50. This is almost a 15% increase in the size of the hexagonal cell spacing with the addition

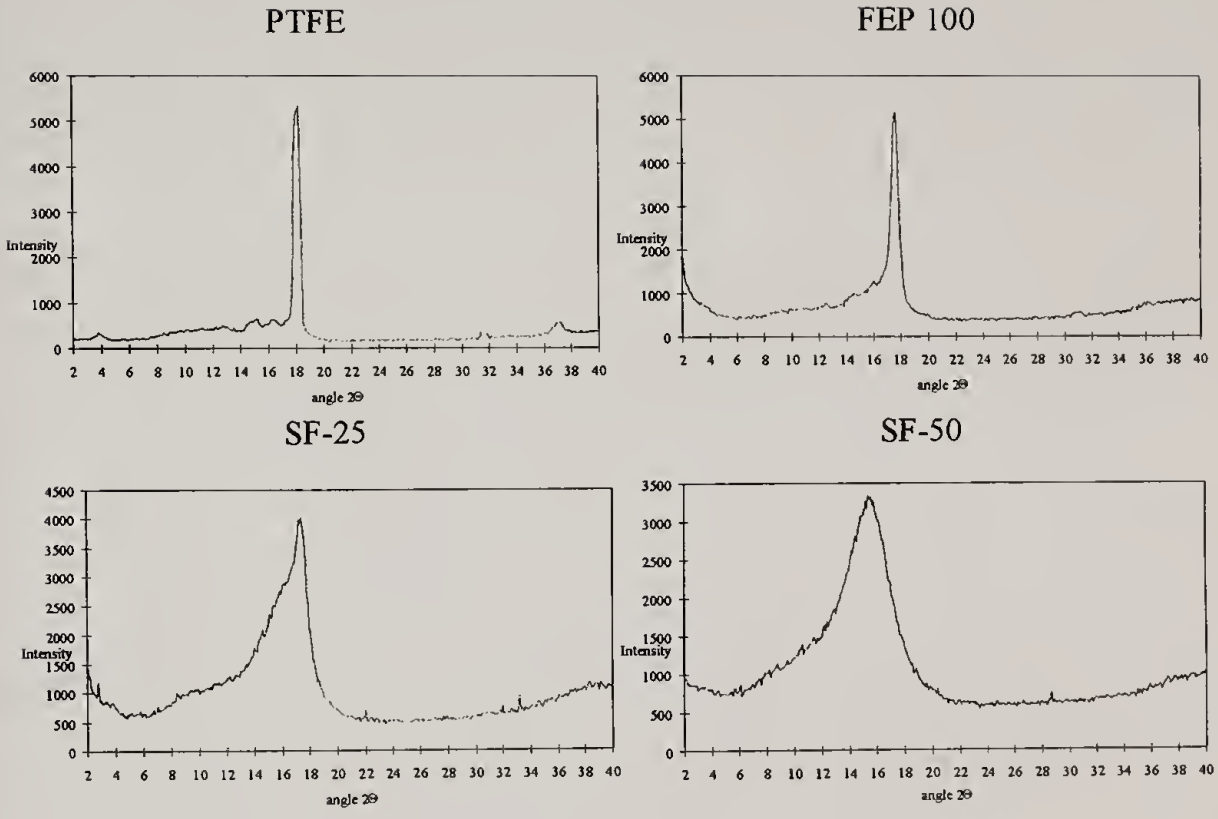

Figure 5.1: Unoriented x-ray diffraction scans: (a) PTFE (b) FEP100 (c) SF-25 (d) SF-50

of 50% HFP. The cross-sectional area per molecule increases by 32%. However, based on the concurrent peak broadening by a factor of 6 compared with the homopolymer half width and the disappearance of the higher angle peaks, the unit cell structure is less ordered and less discrete for the SF-50 compared to the PTFE control structure. The FEP 100

Table 5.1. WAXD data from unoriented samples

	% HFP	2q angle, (deg.)	d_{100}, (nm)	a-value, (nm)	half width, (deg.)	area/mol (nm^2)
PTFE	0	18.1	0.490	0.566	0.6	0.277
FEP 100	13	17.7	0.501	0.577	0.8	0.290
SF-25*	25	17.4	0.510	0.589	2.2	-----
		16.2	0.547	0.635	1.2	0.346
SF-50*	50	15.7	0.564	0.647	3.8	0.367

and the SF-25 spacings follow this trend for the expansion and disorder of the lattice structure.

There is an additional interesting feature observed in the SF-25 sample, fig 5.1c. Another peak is evident at a slightly lower angle, $2\theta = 16.2°$, than the main peak at 17.4°. This doublet may represent two populations of crystals corresponding to HFP-rich segments and TFE-rich segments, thereby giving rise to two different spacings. The feature is not evident in the scan of SF-50, Figure 5.1d, possibly because the HFP content is so high that the FEP is very close to alternating in structure based on previous arguments. [7] . Alternatively this doublet may simply be obscured in this sample by the considerable peak broadening.

As mentioned, the Rhinolyzer® imaging software was used on these x-ray traces to determine the percent crystallinity for each sample. As shown in Table 5.2, the PTFE and FEP 100 have crystallinities of 95% and 72%, respectively, as expected from literature. With the introduction of even more HFP into the copolymer, the amount of crystalline domains drops proportionally. In fact, the SF-50 has about half the amount of crystallinity as the homopolymer, PTFE.

Table 5.2. Degrees of Crystallinity

	Crystallinity (%)
PTFE	95
FEP100	71
SF-25	53
SF-50	42

Fiber X-ray Diffraction Patterns

The WAXD patterns from the four oriented materials are shown in Figure 5.2. These oriented patterns have the advantage of being able to clearly delineate between intra and inter molecular changes as function of HFP content. Figure 5.2a is the familiar x-ray fiber diffraction pattern from PTFE. The three sharp equatorials diffraction signals are the characteristic 100, 110 and 200 of the well-ordered two dimensional hexagonal lattice associated with the packing of the PTFE helices. They have the same spacings as those measured on the x-ray diffraction scan (Figure 5.1a; Table 5.1) and confirm our original indexing assignment. Sharp diffraction signals are also observed on layer lines with spacing 0.279 nm and 0.244 nm (errors ±0.001 nm) which correspond to the 7th and 8th layer lines of a 1.95 nm c-spacing. These diffraction signals prove that the chain

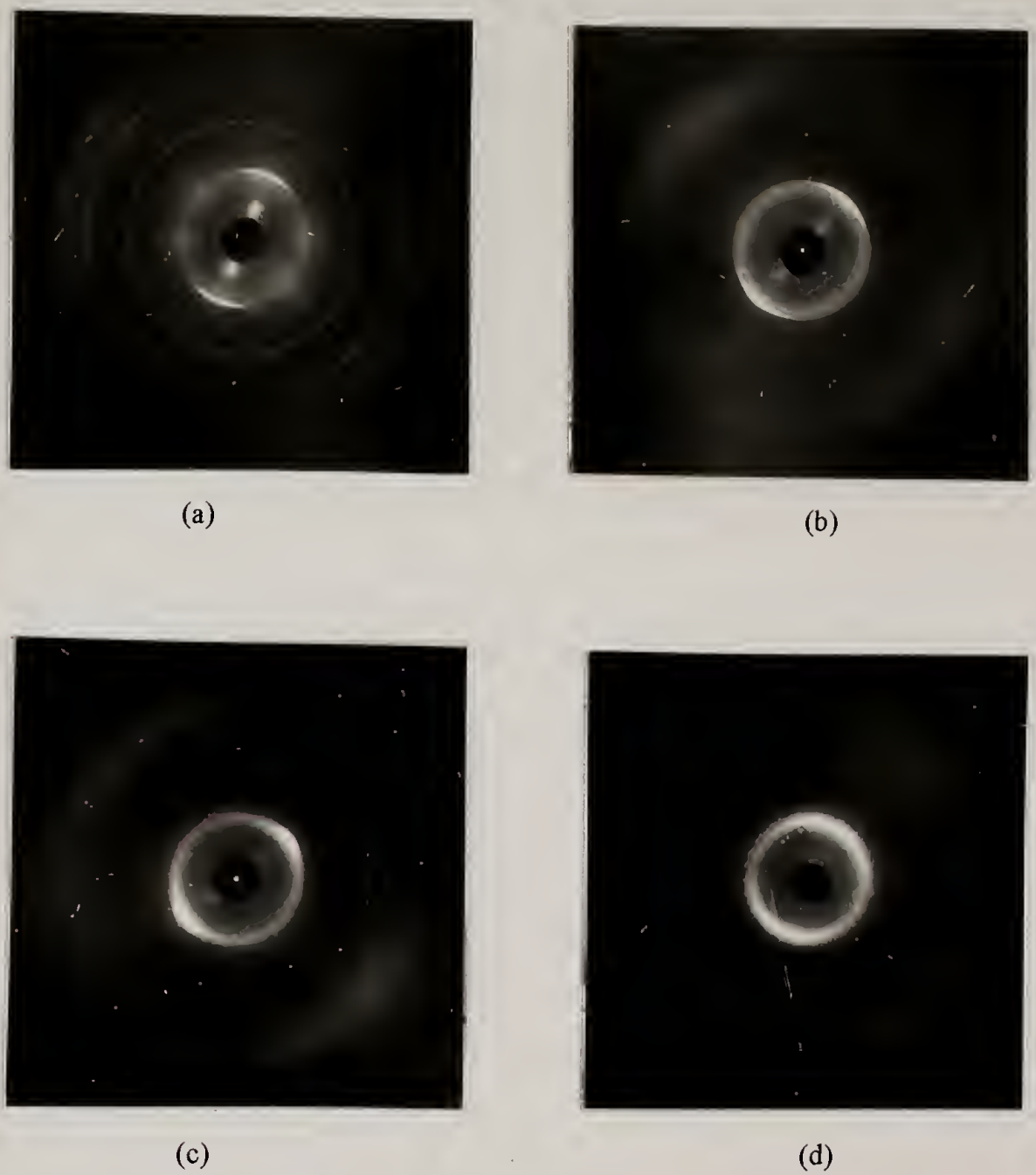

Figure 5.2:X-ray fiber diffraction patterns from oriented PTFE and copolymers (draw direction vertical). (a) PTFE showing the three sharp, characteristic (100, 110, 200) equatorial diffraction signals of the hexagonal lattice with a = 0.566 nm. Sharp diffraction signals also occur on the 6th and 7th layer lines confirming a 15/7 helical conformation. The right-hand half of the pattern contains a calcite calibration ring. (b) 13 mole % HFP (FEP 100) copolymer; note the 6th and 7th layer line diffraction signals are diffuse and almost merge; an unoriented ring on the inside edge of the 100 has appeared. (c) 25 mole % HFP copolymer (SF-25); only the 100 equatorial signal remains and the relative intensity of the unoriented inner ring has increased; the relative intensity of the diffuse layer line diffraction has decreased. (d)50 mole % HFP copolymer (SF-50); the orientation is lost and the 100 and inner ring have merged.

has a 15/7 helical conformation since strong diffraction signals occur on these two layer lines. (The 13/6 helical conformation, that exists at lower temperature, has strong contributions on layer lines with spacing 0.282 nm and 0.241 nm, and a different a-value). The strong diffraction on the 7th and 8th layer lines of the 15/7 PTFE helix reveals the sub-periodicity, between 1/7th and 1/8th of the c-repeat period, i.e., 1.95/7.5 (= 0.26 nm), corresponding to the axial projection of two C-C backbone atoms; the PTFE structure is a slowly precessing planar zigzag. The presence of these two sharp and intense diffraction signals demands that the helical conformation is both regular and has a defined c-repeat. In the case of the incorporation of 13 mole % HFP (FEP 100) the characteristic set of three (100, 110 and 200) equatorial diffraction signals remain, as shown in Figure 5.2b, although they are marginally broader and weaker. The hexagonal lattice d100-value (0.490 nm) matches that of Figure 5.1b and Table 5.1. In addition, a second component is evident; on the inside edge of the 100 diffraction arc, an unoriented, broader diffraction ring appears centered on a value of 0.540 nm. This can be attributed to a disordered component that is less readily oriented than the crystalline component. More important however, is the observation that the sharp 7th and 8th layer line diffraction signals (of PTFE) have become diffuse, to the extent that they have almost merged and now appear has a near-meridional diffuse band of diffraction (see Figure 5.1b). Thus even in the crystalline component, the effect of the incorporation of 13 mole % HFP has destroyed the precise 15/7 helical conformation, but the molecular chains still pack in a slightly expanded (2%) two dimensional lattice. This suggests that there are fluctuations in the rotation angle between contiguous monomers as a consequence of the insertion of HFP. These trends continue with the 25 and 50 mole %

HFP materials, as shown in Figures 5.2c and 5.2d. In both cases the higher-orders of two dimensional reciprocal lattice disappear and the 100 signal becomes broader and moves to a larger spacing (Table 5.1) with increasing HFP content. The inner diffraction ring increases in relative intensity, compared with the 100 signal, and the doublet merges in the case of the 50 mole % HFP and orientation is lost; the diffuse 0.26 nm layer line diffraction weakens and becomes progressively less oriented. These results reflect the transformation of regular helices into randomly decorated rod-like molecules and a consequent weakening of the intermolecular interactions and destruction of the crystalline component.

Conclusions

The structural changes as a function of increasing HFP content, as monitored by x-ray diffraction, can be categorized into four different but related effects. (1) The steady destruction of the regular helical conformation for the polymer molecules. (2) Increase in the lateral packing of the molecules as a result of the bulkier CF3 side chains. (3) The randomly distributed CF3 groups frustrating the crystallization of the molecules. (4) The development of separate semi-crystalline and amorphous components at mole % HFP values as low as 13%.

The incorporation of HFP has caused disruption of the regular helical conformation of PTFE homopolymer, the disorder increasing with increasing HFP content. This is evident from the progressive broadening and weakening of the diffraction signals on the 7th and 8th layer lines. The gentle, regular twist of the helix in the PTFE homopolymer arises from the need to accommodate the fluorine atoms

(Pauling radius 40% larger than the hydrogen atoms in the polyalkanes). The stereochemical interaction causes the chain to be perturbed from the polyalkane planar zigzag into a slowly precessing helical conformation. The main chain bond angle is also affected by the stereochemical constraints and opens up to 116° from the usual value of 109° found in alkanes. In the case of the copolymers the observed merging of the 7th and 8th layer lines into one diffuse diffraction signal with increasing HFP content suggests that substitution of bulky CF3 groups for fluorine atoms has distorted the regularity of the backbone twist. The substitution of the CF3 groups also increases the diameter of the molecule, hence increasing the average intermolecular distance. This is reflected in the expansion of the a-value and the cross-sectional area per molecule.

It is apparent from the x-ray diffraction results that the structure can accommodate up to at least 25 mole % HFP, i.e. one CF3 group per eight backbone carbon atoms, without substantial change in a-value of the two dimensional hexagonal lattice. However, even at 13 mole % HFP, there is measurable changes in the helical conformation, molecular packing and degree of crystallinity and an amorphous component begins to emerge. The distortions of the PTFE chain conformation with increasing copolymer content can be usefully contrasted with the changes in the homopolymer as a function of increasing temperature. Above ~30°C the PTFE homopolymer begins to twist in an irregular manner. This leads to a deterioration in the precise 15/7 helical conformation and hence causes the strong layer line diffraction signals to broaden and merge in similar fashion to that observed on increasing HFP content. However, in the case of PTFE, the two dimensional hexagonal packing remains intact, apart from an increase in the a-value. We believe this is because the semi-mobile

chains behave as rod-like entities, which still pack in a two dimensional hexagonal lattice. Hence a useful comparison may be drawn between lattice disordering resulting from thermal effects or from inclusion of bulky side groups.

Also, based on image analysis, it is evident that the degree of crystallinity decreases with the incorporation of HFP. As the chain becomes less regular it becomes less crystallizable. In addition the stability of the crystals that are formed is lowered by increasing incorporation of HFP as shown by the drop in melting points with increasing HFP content (Chapter 4).

The effect of copolymerization is to disrupt the regularity of the normal PTFE helical conformation and hence make the molecules less crystallizable. This is reflected in the lower crystallinities seen with increasing HFP content. In the crystalline fraction this disrupts periodicity in the chain direction and, furthermore, the bulky CF3 groups cause lattice expansion and disorder in the two dimensional hexagonal array into which the molecules pack. This disorder is noticed in the drop in the melting points with increasing HFP content, discussed in chapter 4. It is considered that the de-stabilization of the crystalline phase is responsible for the desired increased solubility of these materials compared with PTFE homopolymer.

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CHAPTER 6

COATING PROPERTIES

Introduction

Material properties help to determine boundaries of operation, but to understand how the material behaves as a coating, more specific measurements need to be done. Adhesion is probably the most important issue at hand in describing coating performance. There are a number of techniques available for measuring the energy it takes to delaminate a polymer film from a substrate and the goal here is to use the technique which best isolates this energy. The goal is difficult to fulfill for such thin films (~10- 50μm) since the film can deform during the delamination process much more easily than a thicker film. If the adhesion energy is large, this can lead to problems with even thicker films. The literature is filled with different adhesion measurement techniques for this application. The blister test [1-3], the microscratch test [4], peel tests [5, 6], ultrasonic tests, the scratch/scrape test, and the tape test [7] are a few that are most applicable to the case at hand. However, each has its own disadvantages, whether it be the complexity of the application with the microscratch test or the probability of deformation comprising a good portion of the energy of peel measured in the peel test. What has become the most attractive technique for this purpose is the self decohesion test method developed here in this laboratory by C. Bauer and R.J. Farris. [8]

In order to understand the applicability and value of these new FEP copolymers as protective coatings, barrier properties should also be measured. Permeability and

diffusion are the main mechanisms of transport through films of this type and are therefore of interest here. Permeability can be measured directly, whereas, diffusion can be measured indirectly via corrosion testing. The pressure differential method was chosen for the permeability measurements [9], while corrosion testing was carried out using an Atlas test cell set-up. [10]

Adhesion

Self Decohesion Test

The self-decohesion theory is based on an energy balance approach to determining adhesion energy from the internal energy of an isotropic material in a state of plane stress [11]. Once again, coming in only a few film thicknesses from the edge, the coating and substrate are not interacting mechanically and, therefore, experiences no interfacial stresses except near an edge. By introducing a crack defect, or an edge, as show in Figure 6.1, delamination will occur if the coating stress and the film thickness translate into enough energy to overcome the adhesion energy. The stored energy per unit area, U_A, in a coating is given by the following relation which originates from the linear elastic, isotropic nature of the coating material.

$$U_A = \frac{\sigma^2 t(1-\nu)}{E} \qquad (6.1)$$

Here the Young's modulus and poisson's ratio are given by E and ν, respectively, while the film's thickness and in-plane residual stress are given by t and σ, respectively. As stated, when a crack is introduced, the coating will spontaneously delaminate if the stored energy is high enough. To avoid non-uniform stress

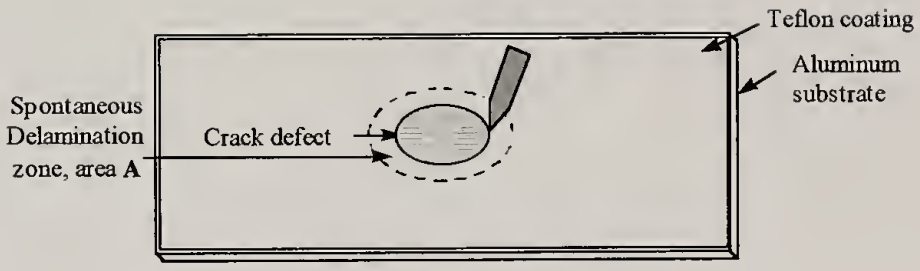


Figure 6.1: Self Decohesion test example

concentrations that can develop at the tips in a straight crack, a circular crack geometry is used, as shown in Figure 6.1. If the coating will delaminate to a larger radius circle. By using polar coordinates to describe the stresses and delamination area, the difference in energy between the bonded and debonded state can be calculated. This difference is related to the surface energy of adhesion. The resultant equation of this derivation is given here, solved for the adhesion energy.

$$\gamma = \frac{\sigma^2 t[a^2(1-\nu^2)]}{E[b^2(1-\nu)+a^2(1+\nu)]} \qquad (6.2)$$

The new variables that appear are a and b, which refer to the radius of the introduced crack and the radius of the delaminated area, respectively. This particular approach allows the determination of the adhesion energy without imposing any external force or causing any measurable film deformation.

Experimental

Coatings were prepared as described in Chapter 3, focusing on the thickest films achievable for the SF-25, SF-50, and AF1601. By observing equation 6.1 for the energy of adhesion, four variables are required; σ, ν, E, and t. The stress, σ, was measured using holographic interferometry and the modulus, E, was also measured by tensile testing, both described in Chapter 4. The thickness measurement was made using the Mitutoyo thickness gauge described in Chapter 3. A literature value was used for the poission's ratio of the FEP of 0.48 and Teflon® AF's value was assumed at 0.48. [12] These values are all summarized in Table 6.1. All three films were prepared and cracks were made in the coatings using an exacto knife. The circular shape was achieved by

carefully cutting around a small steel disc with a 9 mm diameter, resulting in a defect of radius 9.15 mm.

Table 6.1: Material Properties for Adhesion Calculation

Polymer	Modulus (MPa)	Poisson's ratio	σ (MPa)
SF-25	727	0.48	2.2
SF-50	670	0.48	0.0
AF1601	992	0.48	31.0

Results

For the case of the SF-25 and SF-50, delamination did not occur after the crack was introduced into the coating. Therefore, under standard temperature and pressure conditions, these coatings will not delaminate or catastrophically fail in adhesion. Teflon® AF 1601, on the other hand, delaminated to a radius 1.77 mm larger than the initial crack radius. This area corresponds to an adhesion energy of 20.7 J/m^2 for AF 1601 on glass.

The cause for the discrepancies in the coating behavior between the SF polymers and the AF can be traced to the large differences in their residual stress values. By observing the residual stress values in Table 6.1, the SF-25 and SF-50 have residual stresses at 2.2 MPa for SF-25 and SF-50 is stress-free, whereas the AF1601 has 31 MPa residual stress. This will translate into a much higher stored energy for AF 1601 and subsequent instability with crack defects. In order to obtain quantitative values for the adhesion energies of SF-25 and SF-50, different methods of aggravating the stress state were used, as follows.

Beam bending test

Beam bending is a technique used to measure coating adhesion in some instances. [13, 14] Here it used to superimpose a larger stress in the coating material by straining the film. Using a simple cantilever beam set-up with one fixed end as the boundary condition, the governing equation for the stress in the outer fibers of the beam becomes

$$\Delta\sigma_c = \frac{E_c t_b}{2\rho} \tag{6.3}$$

where,

$\Delta\sigma_c$ = stress in the outer fibers or coating

E_c = modulus of the outer fibers or coating

t_b = thickness of the entire beam

ρ = radius of curvature = $l^2/2\delta$, for $\rho >> 1$

So by performing this bending experiment on a beam coated with the fluoropolymer, the stress will be increased by σ_c. Then the self decohesion test can be attempted on the stressed film.

Experimental

SF-25 and SF-50 were blade coated onto aluminum beams 1 cm x 15 cm x 1.5 mm, of thickness 71 and 68 μm, respectively. The samples were then mounted into a holder with a clamp on one end and a caliper on the other, 10 cm apart. The caliper was first set to a reading of 0.0 mm with the sample held straight in the holder with the caliper probe resting on the coating surface. Subsequent, rotation of the caliper caused

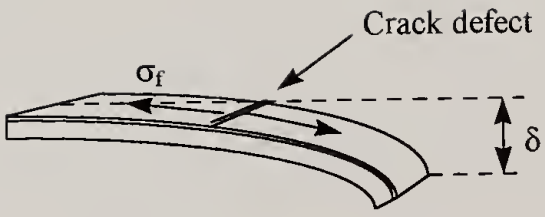


Figure 6.2: Beam bending set-up

the probe to push down on the free end of the beam. The total deflection, δ, as shown in Figure 6.2 was read from the caliper. The defect also shown in Figure 6.2 was introduced to initiate delamination either before or after a maximum deflection of 27 mm was reached.

Results

No delamination occurred in either sample under the large deflections put on them. Using the modulus and thickness values already given, a deflection of 27 mm, and beam length of 10 cm, the added stress could be calculated for the films using equation 6.3. The following table shows the results of the calculated stress and the estimated adhesion energy using equation 6.1.

Table 6.2: Stresses and Estimated Adhesion from Beam Bending

	$\Delta\sigma_c + \sigma$ (MPa)	Adhesion Energy (J/m^2)
SF-25	5.1	>1.32
SF-50	2.7	>0.38

Low temperature test

All materials have some sort of response to thermal exposure which can be expressed in terms of its coefficient of thermal expansion, α. For bilayer systems, as is the case for a coated substrate, the different layers can have different thermal expansion coefficients. The materials interact with one another through the interface and, as described above, the coating will have a stored energy or residual stress at ambient

conditions due to this interaction. Since stored energy is incremental, equation 6.1 can be modified to show the thermal expansion effect on stored energy in a coating material.

$$U_A = \frac{(\sigma + \Delta\sigma_T)^2 t(1-\nu)}{E}, \Delta\sigma_T = -\frac{E(\alpha_c - \alpha_s)\Delta T}{(1-\nu)} \tag{6.4}$$

where,

$\Delta\sigma_T$ = change in stress as a result of a temperature change

α_c = in-plane CTE of coating

α_s = CTE of substrate

Polymers, in general, have much larger coefficients of thermal expansion than metals or glass and will therefore have a more pronounced response to thermal input. The thermal expansion coefficients for the materials used here are listed in Table 6.3.

Table 6.3: CTE's of coatings and substrates

Material	CTE (ppm/°C)
SF-25	130
SF-50	130
Aluminum	23.1
copper	16.5
glass	2.5

The situation of interest here is when the polymer/substrate system is cooled down to very low temperatures. This would produce a positive change in the stress state of the coating, which adds energy to the film. If cooled down low enough, the coating may delaminate on introducing a defect.

Experimental

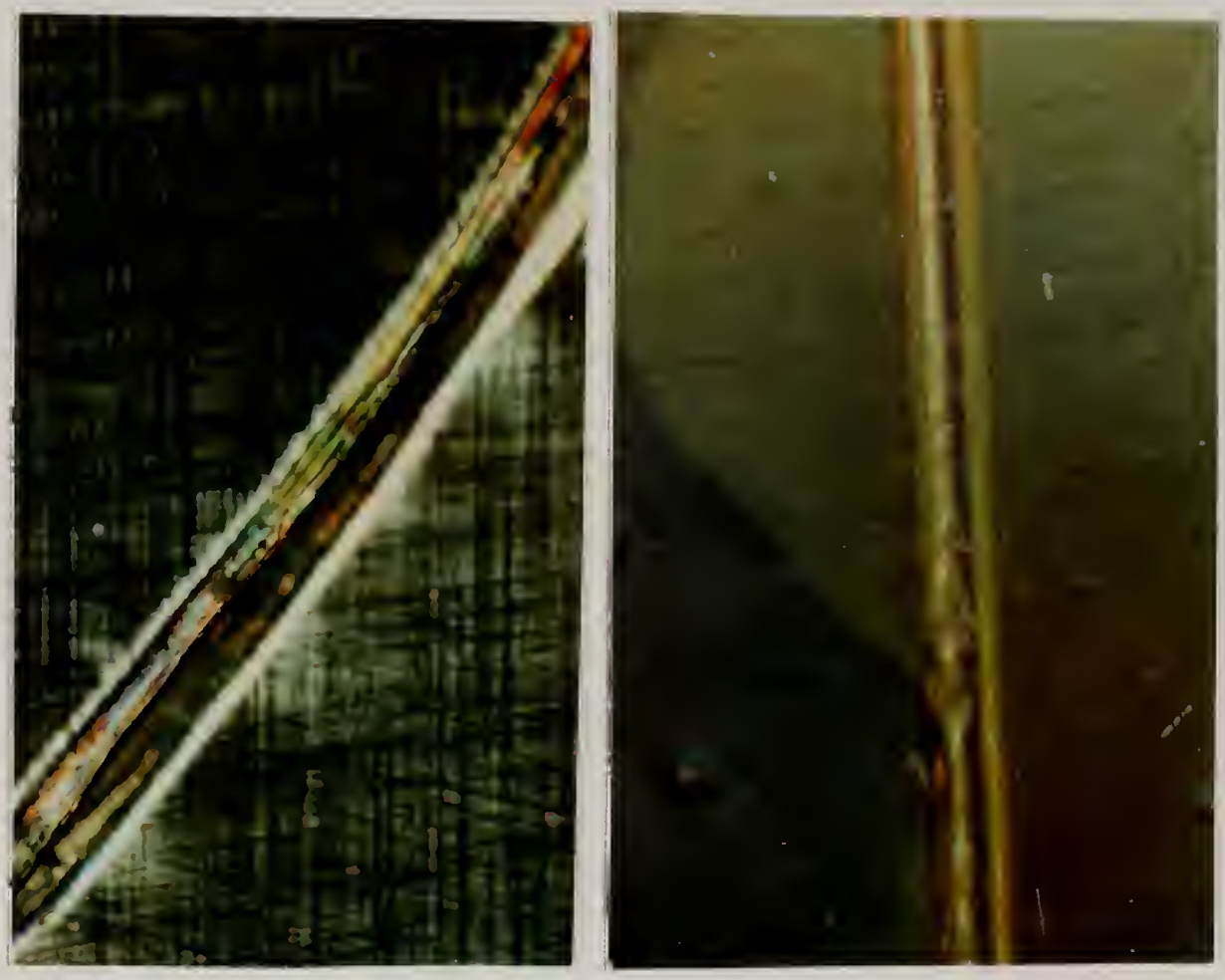
Both the SF-25 and SF-50 were coated onto Al, Cu, and glass at roughly 60 μm thickness. The samples were then brought down to liquid nitrogen (LiN_2) temperature of -195°C. Cracks were cut into the coatings both before and after reaching the -195°C.

Results

Even though the samples were eventually completely submerged in LiN_2, delamination did not occur in all cases, except for SF-25 on Cu. As can be seen in Figure 6.3 a and b, the sample coated on Al showed no delamination under magnification, however non-uniform delamination did occur with the coated Cu sample. Upon further inspection, this particular coating went from a clear coating before low temperature delamination, to a yellow film with a shiny copper underside. Therefore, it is safe to assume that the delamination failure occurred cohesively in the copper, not at the copper/SF-25 interface. For all coatings, the adhesion energy is greater than the energy stored in the film at -195°C, calculated from equations 6.4. Table 6.4 shows the properties used in this calculation and the resulting stress and estimated adhesion energy. The stresses calculated are higher than the ultimate stresses measured at room temperature. Even though the ultimate stress may increase with a decrease in

Table 6.4: Adhesion energy Estimations

Sample	σ (MPa) @ -195°C	γ (J/m^2)
SF-25 on Al	35.0	>53.4
SF-50 on Al	30.3	>42.8



(a) (b)

Figure 6.3: (a) Al sample (b) Cu sample - both low temp. test

temperature, it probably does not to the extent shown. It is more likely that the thermal stresses result in yielding, limiting the strain energy. So these energy numbers calculated are just a rough estimate of what the adhesion energy might be.

Multiple layer test

Another attempt at stress aggravation was attempted by coating a more highly stressed layer onto the FEP coating. Again the stored energy is additive and as long as the top coating adheres well to the FEP, the energy acting at the FEP/substrate interface is the sum of the two coating energies.

A couple of problems needed to be addressed: finding a coating with high stresses that could be made at moderate temperatures, and getting a material that would adhere to the FEP. Polyimide materials were ruled out as candidates because of the high temperature curing required to form the highly stressed coating. Gelatin-type materials, however, could be crosslinked at room temperature. The resultant shrinkage stresses would possibly be enough to cause FEP delamination from glass. Based on previous gelatin work done in this laboratory, poly (vinyl alcohol), PVOH, was chosen as the best candidate. [15] This material physically crosslinks by hydrogen bonding. After the solvent (water) is removed, the film has in-plane stresses as high as 40 MPa and a modulus estimated at 1 GPa based on information from Air Products. [16, 17] Holographic interferometry was used, as described in Chapter 4, to verify the stress level. Measurements showed isotropic stresses of 34 MPa at 22 in. Hg vacuum pressure.

In order to enhance the adhesion of the PVOH to the FEP, in this case SF-25, the surface of the FEP was exposed to a radio-frequency oxygen plasma and subsequent metal deposition. [18-20] The plasma etching alters the surface of the FEP by both mechanical etching or ablation (creating more surface area) and by chemical reaction which deposits functional groups onto the FEP surface (primarily oxygen in this case). This is enough to enhance adhesion of a thin metal layer onto the FEP. X-ray Photo-electron Spectroscopy (XPS) was used to determine the extent of etching before metal deposition. Then a thin layer of metal was deposited onto the etched surface of SF-25.

Experimental

Three glass substrates were coated with SF-25, and two out of the three were etched with oxygen plasma for a half an hour at settings prescribed by Jack Hirsch and Meng Hsieh. The samples were stored in an inert N_2 atmosphere. XPS was used to characterize both the plasma-etched and non-plasma-etched SF-25 surfaces. Gold was sputter coated onto one of the etched samples and platinum was evaporated onto the other by Lou Raboin in the Polymer Science and Engineering Microscopy lab. Again the samples were returned to the inert atmosphere.

PVOH was dissolved in HPLC grade H_2O at a concentration of 10 % by weight. Dissolution occurred after stirring for 2-3 hours at 90°C. The solution was allowed to cool and was coated onto the two modified SF-25 coating surfaces. The samples were air dried for one day and subsequently set in a vacuum at room temperature to fully evaporate the water. Finally, the circular defect was introduced into each sample.

Results

The surface analysis revealed by XPS at a sampling depth of ~ 10 Å is summarized in Table 6.5. The plain SF-25 surface shows no impurities at detectable limits. The results are characteristic of the TFE/HFP copolymer, where both the TFE and HFP have F:C ratios of 2:1. The plasma-etched surface shows some chemical modification, indicated by the introduction of ~2 % oxygen. The change in the F/C ratio from 1.99 for the SF-25 to 1.55 for the surface modified SF-25 is due to the chemical reaction but also indicates ablation and maybe some crosslinking.

Table 6.5: XPS atomic concentration results

element	% concentration SF-25	% concentration etched SF-25
C	33.43	38.41
F	66.57	59.75
O	-	1.84

After metal deposition and coating of the PVOH onto the new surface, the circular crack of 9.15 mm radius was introduced. Delamination was observed immediately with the crack delaminating to a larger radius of 11.78 mm. Table 6.6 shows the parameters used for the adhesion energy calculation based on equation 6.2. (Poisson's ratio is estimated.) The corresponding adhesion energy for such behavior is 30 J/m^2. After further inspection of the delamination, it was apparent that the delamination occurred at the PVOH/metal interface. Therefore, it can be assumed that the SF-25 (and SF-50 for that matter) has an adhesion energy to glass greater than 30 J/m^2.

Table 6.6: Adhesion parameters for PVOH

σ	34 MPa
E	~1 Gpa
ν	0.5
t	55 μm
a	9.15 mm
b	11.78 mm

Permeability

Introduction

Passage of a permeant through a membrane is governed by the solubility and diffusivity of that permeant in the given polymer. Ideally, permeability, P, is the product of the coefficients of diffusion, D, and solubility, S, which can be described by Fick's and Henry's laws, $J = -D(dc/dx)$ and $S = c/p$, respectively. (J = particle flux, c = concentration of particles, x = depth of particle penetration, and p = partial pressure)

$$P = DS \tag{6.4}$$

For gases, it is believed that a steady state is reached after diffusion takes place for a period of time at constant temperature.

The two main methods used to measure the permeability are the pressure differential method and the isostatic method.[9, 21] In the pressure differential method, the quantity of gas that passes through the film is calculated from the measured pressure

difference across the membrane, Δp. Alternatively, the isostatic method estimates Q from the change in the gas mixture and flow rate.

For the proposed research, the former method will be utilized. Therefore, the quantity of gas, Q, that passes through the membrane can be expressed in terms of the pressure difference across the film, Δp, the permeability rate, P, cross-sectional area, A, and time of exposure, t, divided by the thickness of the film, x, as shown in equation 6.5.

$$Q = \frac{PAt(\Delta p)}{x} \tag{6.5}$$

Experimental

Test set-up

By using the setup shown in Figure 6.3 and knowing all its parameters, the time can be measured for the pressure transducer to go through a certain pressure change. This enables the calculation of the permeability through the following equation which results from rearranging equation 6.5.

$$P = \frac{Qx}{At\Delta p} \tag{6.6}$$

As one can see, the volume of gas through the film, Q, is known from the apparatus as well as the area. The thickness of the film was also measured, leaving the time and the pressure change as the two unknown variables. The gases used in this investigation were carbon dioxide and air. This allows determination of the protective capability of the coatings in standard environments.

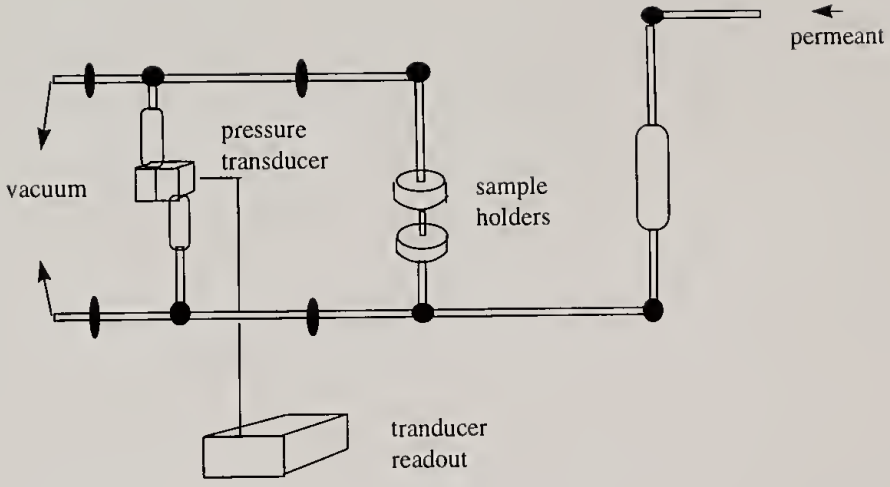


Figure 6.4: Gas Permeability apparatus

Sample Preparation

Film samples of SF-25, SF-50, and AF 1601 were prepared as in Chapter 3 of varying thickness, averaging around 70μm. Two samples for each run were then cut and placed in the sample holders. The gas, CO_2 or compressed air, was then opened up to the samples and allowed to flow through the system constantly over a 1-2 week sampling time. One measurement was taken per day, whereby the pressure transducer was closed off from the vacuum. This effectively trapped a vacuum on the downstream side and forced the volume of gas into the confined volume between the sample holder and the transducer. The time that it takes for the pressure transducer to read a pressure change of 0.5 mm Hg was then recorded and the permeability calculated using equation 6.6. The long sampling period is required to allow the sample to reach steady state permeation in the first few days and then obtain a week's worth of constant time readings.

Results and Comparison to literature

Table 6.7 shows the results of the testing conducted. The resulting permeability is given in barrer which is equivalent to $\frac{cm^3 cm}{cm^2 (cmHg) s} x10^{-10}$. The apparatus parameters are as follows: V = 0.0566 cm^3 and A = 2.27 cm^3. [22] Upstream pressure varied from 50 psi-80 psi. This data can be compared to existing data in the literature for similar thermoplastics, listed in Table 6.8. It is clear that the solution cast FEP samples have

Table 6.7: Permeability Results

		CO_2			comp. air	
	x (μm)	t_{avg}	P (barrer)	x (μm)	t_{avg}	P (barrer)
SF25,25°C	156	8050	**1.25**	-	-	-
40°C	100	2601	**2.60**	142.3	30440	**0.45**
SF50,25°C	104	5685	**1.36**	-	-	-
40°C	-	-	**plasticized**	100	35320	**0.77**
AF 25°C	211	41	**300**	-	-	-
40°C	211	41	**300**	196.7	476	**54.6**

lower permeability rates than the commercial FEP 100. This behavior can be attributed to the higher density measured for the SF polymers (Table 4.1), most likely due to decreased microporosity. AF 1601 is very permeable and will not provide a barrier as a coating, but might be useful as a separation membrane. One other thing to note is the behavior of SF-50 to CO_2. The sample lost any barrier capability at 40°C. However, the behavior did not occur in air. The cause for this discrepancy is probably do to plasticization of the SF-50 by the CO_2 when the temperature is above its glass transition temperature (30°C). Plasticization is the softening of a polymer due to a filler (CO_2) that disrupts the normal packing of the chains.

Table 6.8: Permeability data (barrer) for similar thermoplastics @ RT, CO_2

material	P
SF-25	1.25
SF-50	1.36
FEP 100	10.0
AF 1601	300
AF 2400	2800
PTFE	9.90
PVC	0.16

Corrosion testing

Introduction and Background

Corrosion is basically an electrochemical process where the metal is converted into a metal oxide. There are two distinct reactions in this process: the anodic and cathodic reactions. In the anodic reaction, metal ions leave the metal lattice and react in the corrosive medium with which it is in contact to form hydrated cations. In the cathodic reaction, these cations combine with oxygen or water to form hydroxyl ions. As a result, there is a current flow into the metal and this has been found to be equivalent to the rate of corrosion. [23] One way to impede this process is by introducing a protective dielectric coating onto the metal which will prohibit the electrochemical activity.

Many different techniques are available for determining corrosion resistance level of polymer films on metal. [10, 23-27] The characterization of the corrosion behavior, however, is more vague and left up to the interpretation of the observer. [28] In order to keep consistent with current methods used at DuPont to test corrosion resistance, this research utilized of the Atlas Test Cell. This method was originally formalized by NACE, or the National Association of Corrosion Engineers. [10] It is a thorough test method that combines both the corrosive action of vapor and liquid. In addition, the temperature environment can be controlled.

Experimental

Atlas test cell

The Atlas Test Cell set-up used in this investigation is depicted in Figure 6.4. In this particular instance, modifications have been made to detect the onset of corrosion by electrical resistance measurements as shown in the figure. Seals were used to encapsulate the corrosive fluid in the vessel between the coated plates and the glass container. Initially, Gore-tex tape was used for this purpose but was found to be semi-permeable to the corrosive fluid and rubber seals/o-rings were used instead. The fluid itself consists of an aqueous 1M (3wt%) sea salt or NaOH solution, where the concentration was taken from literature. [26]

The coated plates are oriented such that the FEP is on the inside wall of the aluminum plates, thereby being in contact with the corrosive agent. The temperature control is provided through the use of a heating blanket and monitored with a thermometer directly in the solution. The temperatures investigated are those proposed by NACE standards at 22°C and 45°C.[10] The resistance monitoring was carried out by sending an AC current from an oscilloscope source through the electrodes in contact with the aluminum. (A DC current source was found to cause polarization of the fluid.) Readouts of the resistance in the circuit created were measured using another oscilloscope. Initial data showed a very high resistance measurement. In the event of pitting occurring, due to coating breakdown under the corrosive environment, the resistance dropped quickly. The detection of this onset of corrosion was the primary

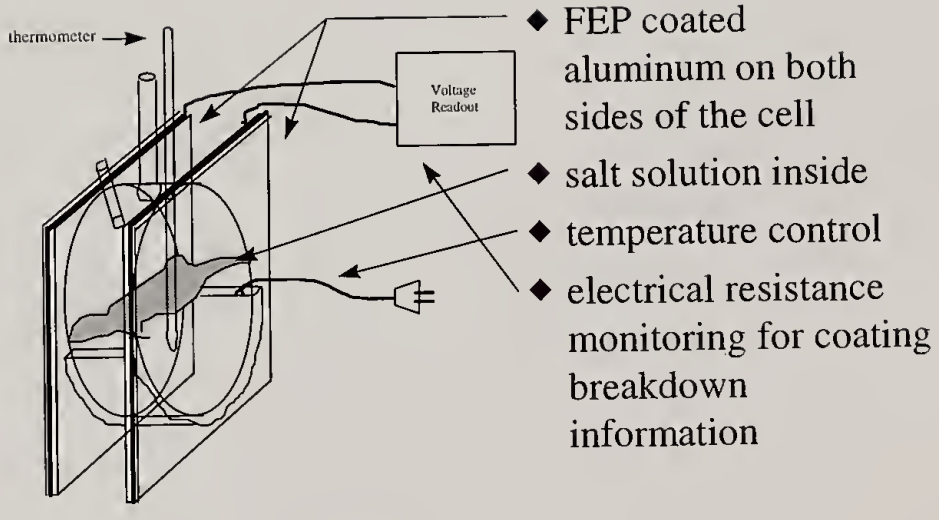


Figure 6.5: Atlas Test Cell Apparatus

resistance dropped quickly. The detection of this onset of corrosion was the primary data sought. Comparisons among the various coatings are made as well as to existing literature.

Sample Preparation

Coatings of intermediate thickness were coated onto aluminum/steel plates by blade coating, as described in Chapter 3. Care was taken to leave enough of an edge to attach an electrode to the metal on both sides of the cell, thereby creating the circuit. The thickness of the films being used are 30-40μm.

Results and Discussion

The data collected on SF-25 and SF-50 coatings on aluminum are given in Table 6.7. The PB (polybutadiene) entry was taken from Touhsaent and Leidheiser's work.[26] The work done in their study was the most consistent with the experimental conditions used here. Other work in the field of flue gas desulfurization (FGD) had much more corrosive media and higher temperatures. [25, 29] The fluoropolymers used in these studies withstood 40 and 90 days respectively with no change to the films observed. Direct comparisons cannot be made due to the extreme differences in the coating thicknesses and experimental conditions.

Table 6.9: Corrosion results

	Temp. (°C)	Time (days)	Status
SF-25	23	230	no change
SF-25	45	4	failed
SF-50	23	230	no change
SF-50	45	1	failed
PB	23	40	failed

Attempts were made to obtain corrosion resistance data from DuPont. Dr. Charles Stewart conducted a DuPont wide literature search for such information, but came up with nothing applicable. The PTFE and FEP commercially available up to this point have not been conducive to forming coatings for such tests.

Summary

The new FEP copolymers reveal exceptional coating characteristics due to the solution processing approach available. The fluoropolymers exhibit adhesion far greater than that of Teflon® AF 1601 (at least 30 J/m^2 compared to 20.7 J/m^2) and stand alone as FEP coatings that require no blending and adhesion promoters to obtain adhesion. The solution processing also results in materials that have higher densities than commercial FEP, regardless of the decrease in crystallinity observed by x-ray analysis. This can be attributed to a probable decrease in microporosity normally exhibited by melt-processed and dispersion-processed commercial FEP. The permeability data obtained reflects this higher density for both of the new fluoropolymers. The corrosion resistance observed is comparable to commercial Teflon® behavior at room temperature (different conditions however). Unfortunately, at only slightly elevated temperatures, the polymers relax through their glass transition temperatures and the corrosion process is accelerated. Again, no real comparable data exists in this field due to the unavailability of equivalent fluoropolymer coatings.

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CHAPTER 7

NANOCOMPOSITE COATING WORK

Introduction

The idea of making a composite material is to combine the properties of two otherwise dissimilar materials and create a new material with ideally tailored properties. The new composite behavior depends on how the two materials interact as well as the individual material properties. Interfacial interactions are of paramount importance because these interactions can be the limiting factor in the composite performance. The advent of nanocomposite materials came about in an attempt to combine two different materials on such a fine scale so as to avoid delamination or incompatibility issues normally found in composite structures. They are desirable in the sense that sharp interfaces can be avoided and the degree of interaction between the dissimilar materials is increased. In some cases, the structure takes on that of two interpenetrating networks in order to mix to a molecular scale.

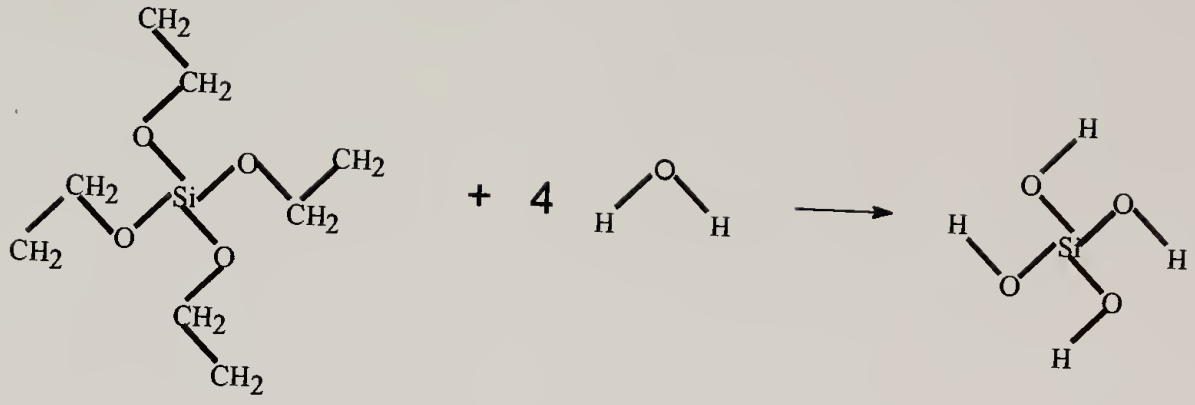
Two materials that could compliment each other well in the form of a composite are ceramics, which are hard and brittle, and polymers, which can be soft and flexible. Due to the very high sintering temperatures required to form a ceramic, and the low melting temperatures of polymers, the likelihood of this happening was very low. However, in the last few decades, sol-gel chemistry, which enables the formation of hard ceramic materials through an aqueous route at room temperature, has become much more well established and understood. [1] This fostered the realization that hard ceramics could be mixed with low melting point polymers to form tough strong

materials. Schmidt conducted research in the area of what he called 'ormosils' or organically modified silanes [2]. Wilkes also did similar work on what he termed 'ceramers' along the same lines [3]. J.E. Mark conducted early nanocomposite work with polydimethyl siloxane (PDMS) polymer networks and in-situ precipitated silicon dioxide (SiO_2). [4]. Bruce Novak later created mutually interpenetrating composite structures through simultaneous polymerization of the polymer and gelling of the ceramic network. [5] Due to the network-forming aspect of these materials, gelling the ceramic in the presence of organics in solution naturally made molecular level composites. In fact, Schmidt and Wilkes were the pioneers in the nanocomposite field. Gianellis and coworkers, later studied mica-type ceramics impregnated with polymers, like PMMA. The PMMA would migrate between the mica platelets and produce small scale mixing [6]. Early work in this area for fluoropolymers, was conducted by Uhlmann involving PTFE with inclusions [7, 8]. With the advent of fluoropolymers in solution came the opportunity to attempt nano-mixing between fluoropolymers and ceramics via the same sol-gel approach. The first obstacle to overcome was the solubility of the silane starter molecules in the perfluorinated solvents.

Typical Sol-Gel Reactions

Typical sol-gel reactions involve hydrolysis and condensation of tetra-ethoxy-silane (TEOS) catalyzed by water or alcohol. (see Figure 7.1) The reaction rate is normally dependent on the r ratio (or ratio of catalyst to monomer), and the pH of the medium. As the silicon dioxide network forms, ethanol is produced as the primary by-product. As this alcohol evaporates, the network shrinks. The drying process must be

Hydrolysis:



Condensation:

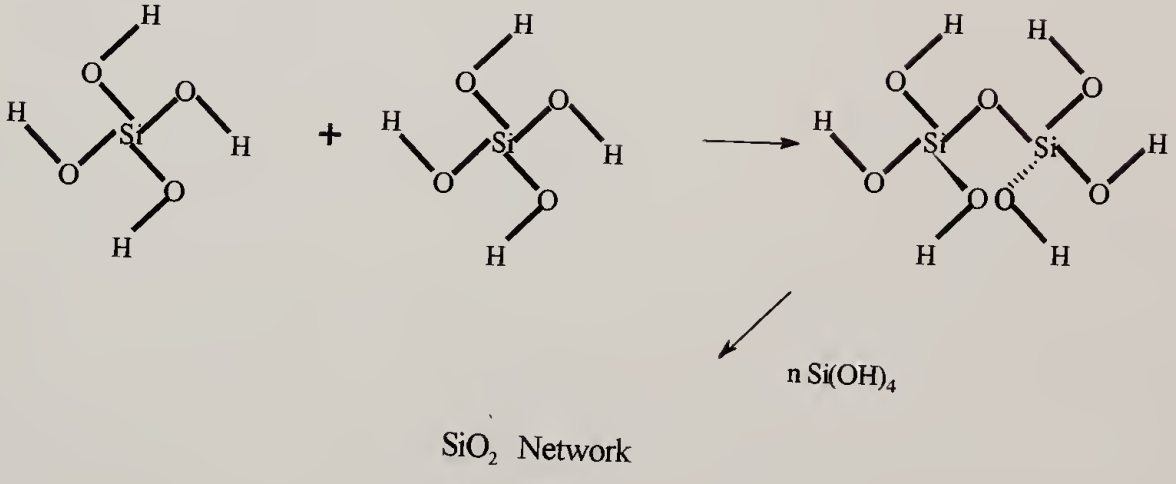


Figure 7.1: Typical Sol-Gel reaction

carefully controlled to avoid shrinkage stresses that could cause unwanted fractures. Slowing the drying process down is usually enough to allow the network to relax into the final product without stress fractures.

Fluoroalkoxy silane Chemistry

In order to perform sol-gel type reactions in the fluoropolymer solution, the silane molecules have to be dissolved in the same solvent. The main criteria for this to occur is that the solute must have some degree of fluorination. Using the chemistry formulated by Dr. Kenneth Sharp and Dr. Michael Michalczek at DuPont [9, 10] (shown in figure 7.2), tetrachlorosilane ($SiCl_4$) can be reacted with a fluorinated alcohol to form the fluoroalkoxy silane. This new molecule is then dissolvable in the PP11 or FC-40 along with the polymer.

Theoretically, trifluoroacetic acid (TFA) can then be added to the mixture, as shown in Figure 7.2, and this will catalyze the sol-gel reaction in the presence of the fluoropolymer. The optimum outcome is to form a continuous network of silicon dioxide, SiO_2, with FEP interpenetrating the pores of the network. This intimate mixing might not only enhance the abrasion resistance by offering a hard ceramic skeleton, but adhesion could also be improved for substrates attracted to SiO_2.

In this particular circumstance, due to the non-polarity and ionic inactivity of both the solvent and polymer, the rate of reaction cannot be controlled by something environmental like pH. The only real control of the rate of reaction is through the architecture of the fluoroalkoxy group. By designing a fluoroalkoxy group that is

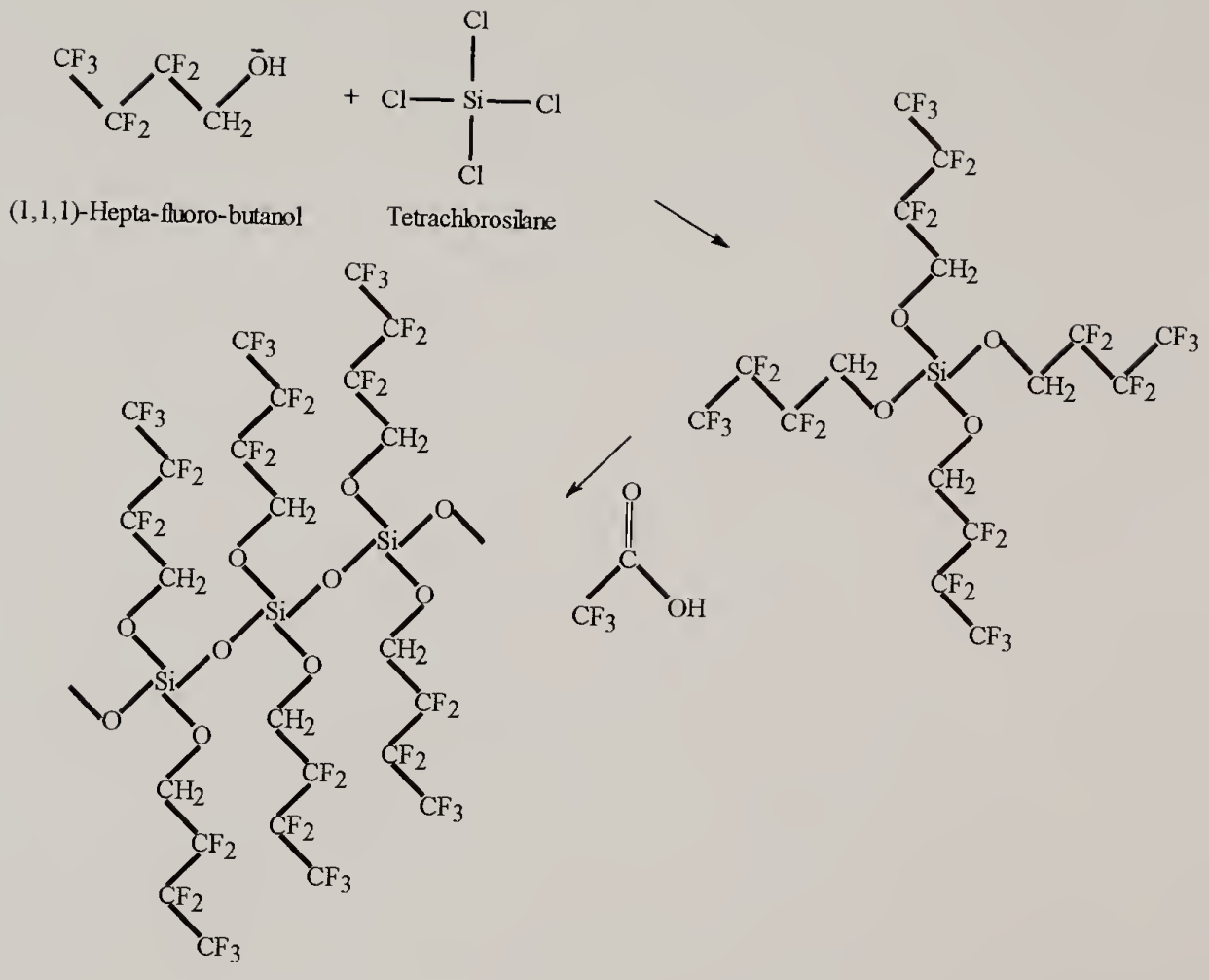


Figure 7.2: Fluorinated Sol-Gel reaction

sterically susceptible to an attack by a catalyst, the reaction may proceed more quickly and completely.

Experimental

Materials

Hepta-fluoro-butanol (HFB) and tri-fluoro-ethanol (TFE) were the two alcohols being used in the formation of the fluoroalkoxy silane. $SiCl_4$ was used as the starting silane, which was subsequently modified to form a fluoro-butoxy-silane (FBS) or fluoro-ethoxy-silane (FES) by reaction with the HFB or TFE, respectively. Structural identification of the product was provided by Dr. Michael Michalczek of DuPont in the form of NMR spectra for each.

Procedures

The HFB and TFE were first by distilled to remove any stabilizers added in packaging. NMR was used to confirm proper products. The fluorinated silanes were then formed by a silane addition reaction, where the silane was added to a stoichiometric excess of the alcohol in a reaction vessel kept at 0°C. After all of the $SiCl_4$ was added (dropwise), the reaction was allowed to proceed and the system was slowly warmed to room temperature, usually overnight. Again, NMR was used to confirm fluorinated silane products.

Finally, the fluoroalkoxy silane was gelled using tri-fluoro-acetic acid (TFA) at an *r* ratio of 4:1, catalyst to silane. This gelation was done both neat and in the presence of a fluoropolymer solution.

Making Composite Coatings

Many different combinations of solvent, fluoroalkoxy silane, and fluoropolymer were investigated to determine the miscibility limits for the composite. The solvents tried were PP11, FC-75, and FC-40. FBS and FES were the representative silanes, and SF-25 and SF-50 the fluoropolymers. All of the mixtures were spun-coat onto glass and the systems were judged based on visual appearance and coating quality. If the coating appeared cloudy, it was a sign of undesirable phase separation of small gelled silane particles.

Results

Figures 7.3-7.8 show the NMR data which verify presence of the products sought after in the distillations. Figures 7.3 and 7.4 are spectrum of the two fluorinated alcohols before silation. Figures 7.5-7.8 show the fluoroalkoxy silane spectrum. Spectra taken from both materials made in this laboratory, as well as at DuPont, are given with the DuPont data being the control.

Table 7.1 shows the ranges of concentrations studied for each of the combinations of polymer, silane, and solvent described above. Of all of the mixtures attempted, the only system that retained homogeneity after coating was SF-50 in PP11 with FBS added. Evidence of phase separation in the other systems has been documented and measured by microscopy at DuPont from Dr. Stewart's laboratory. [11]

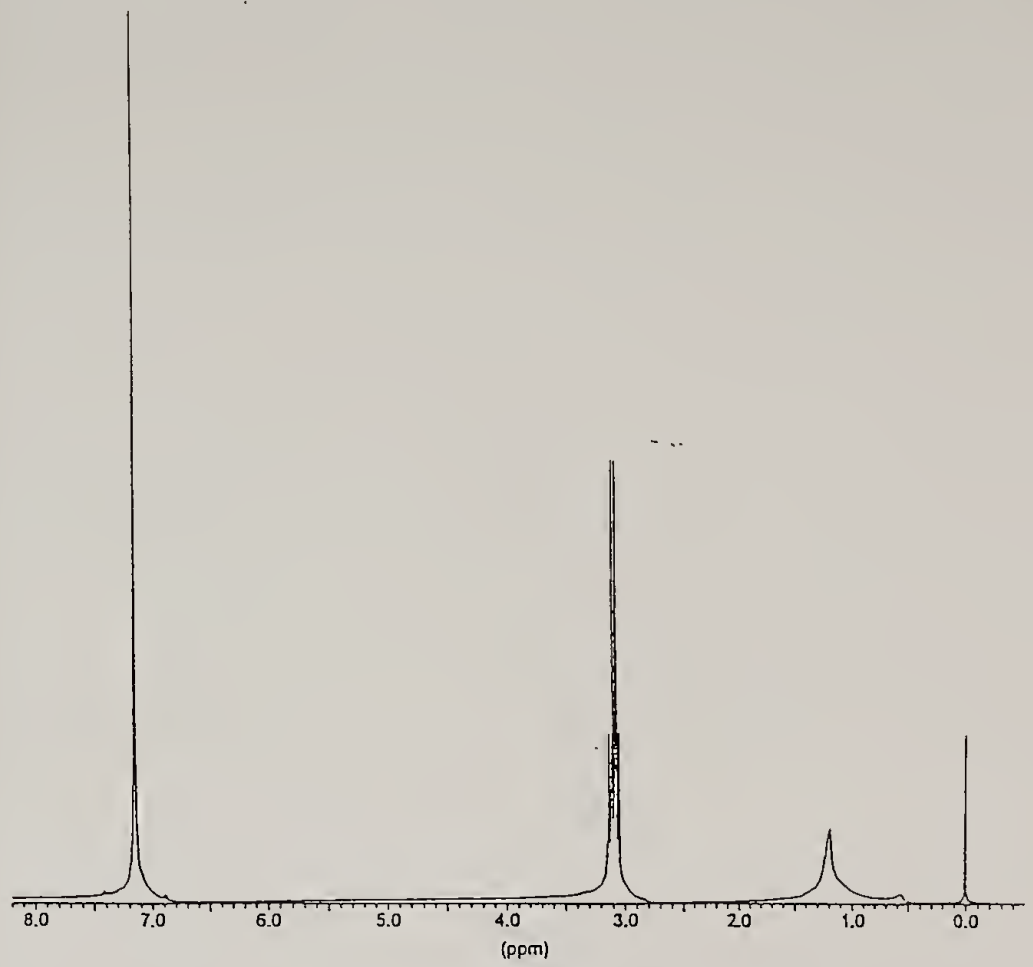


Figure 7.3: NMR of tri-fluoro-ethanol

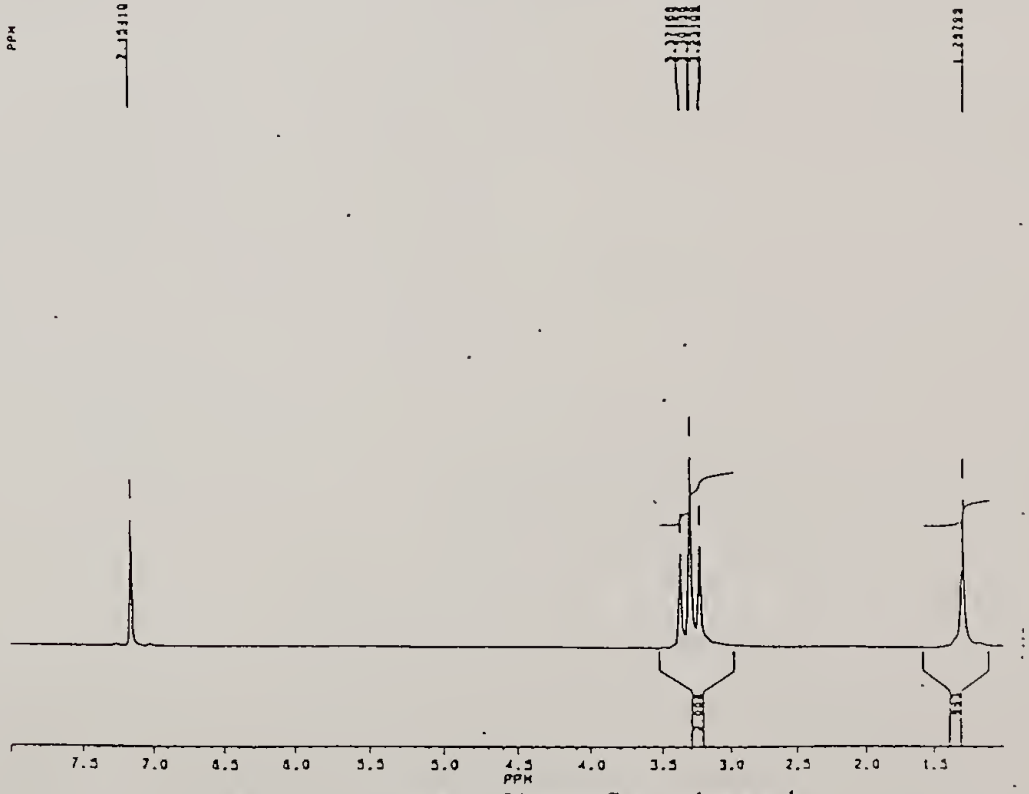


Figure 7.4: NMR of hepta-fluoro-butanol

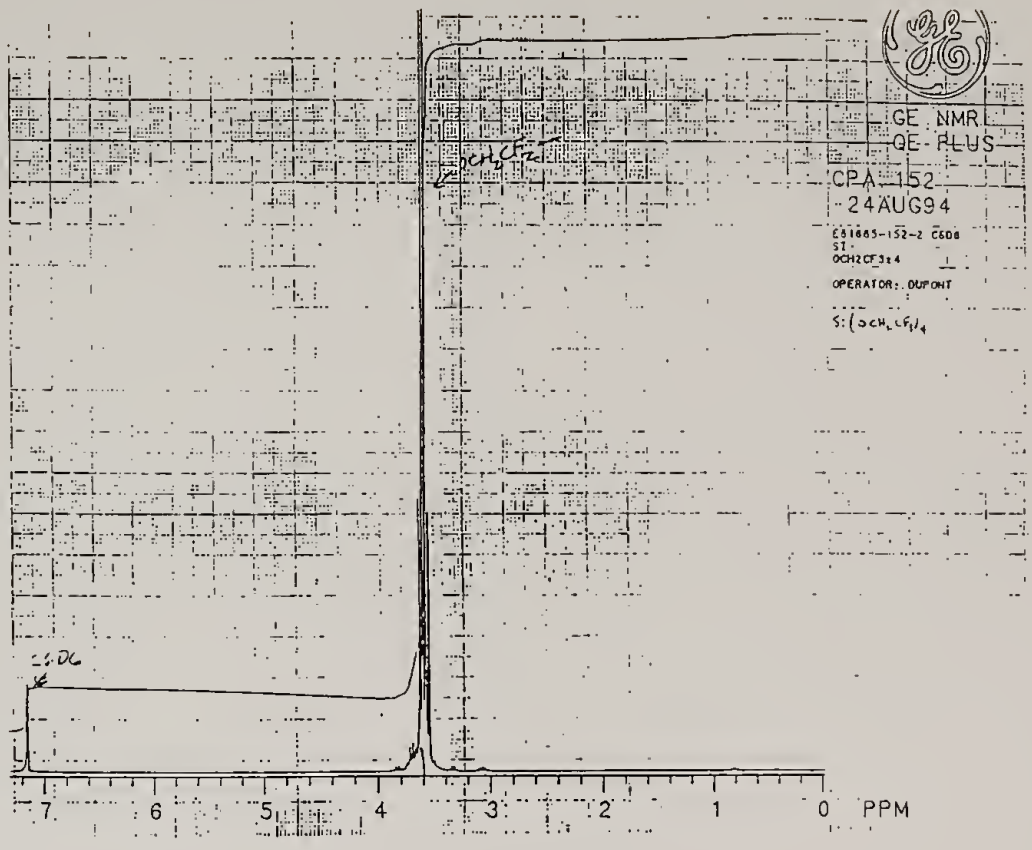


Figure 7.5: NMR of FES (DuPont control)

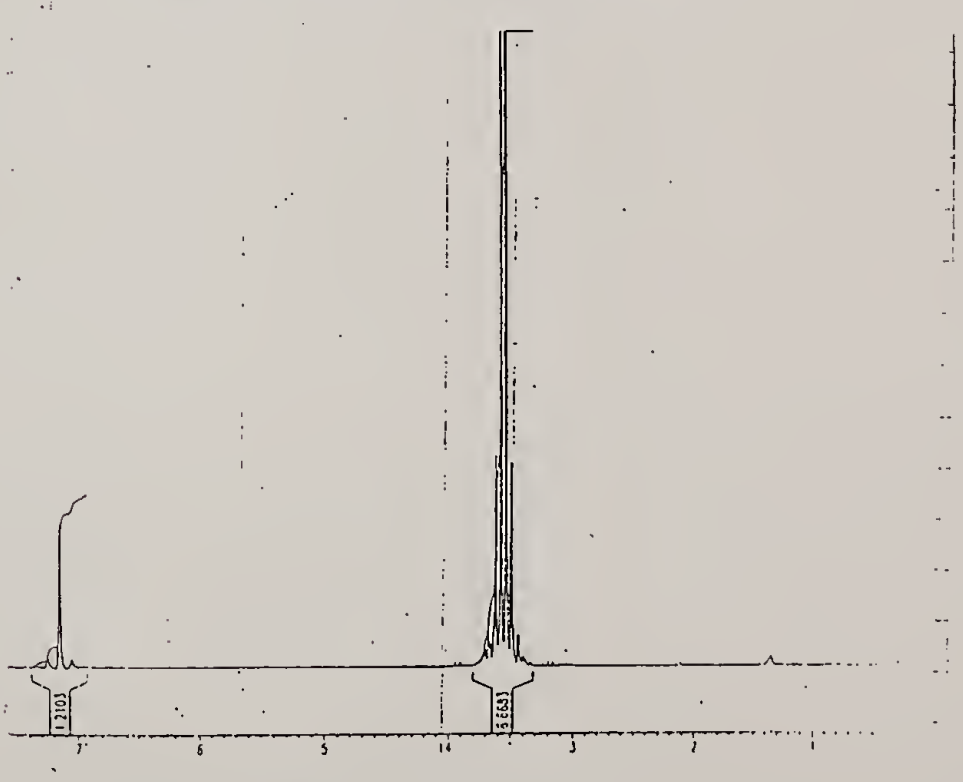


Figure 7.6: NMR of FES

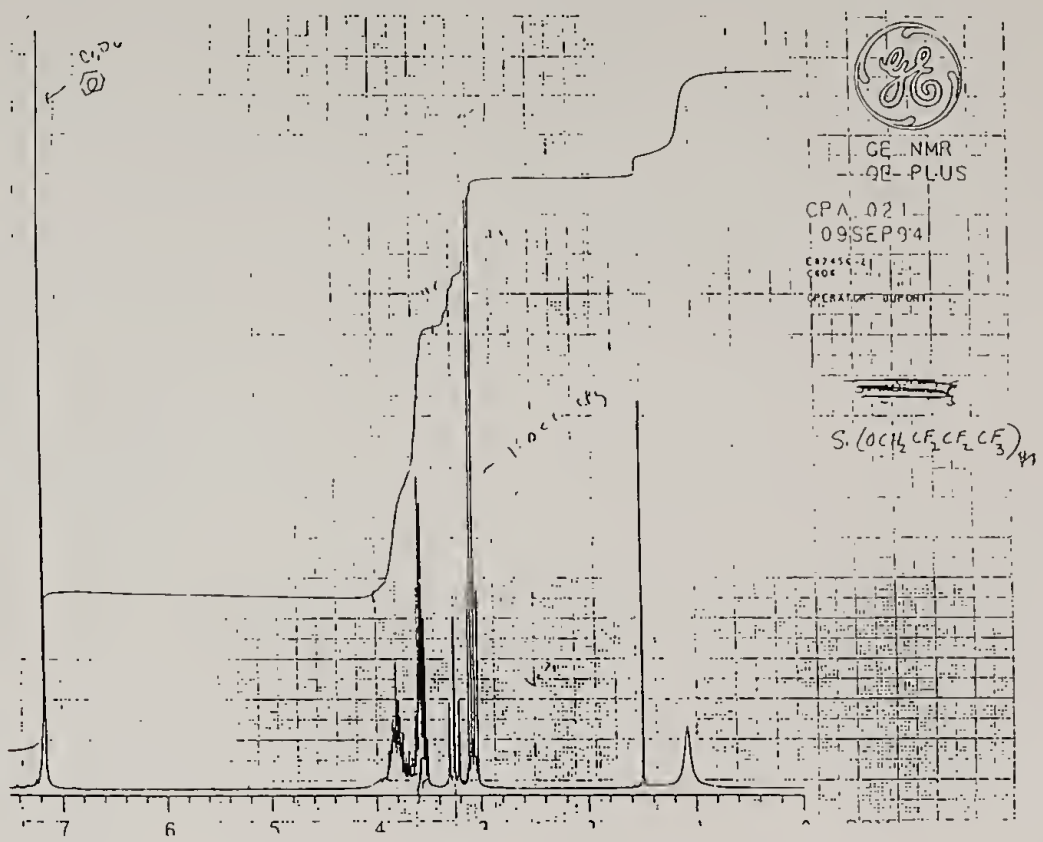


Figure 7.7: NMR of FBS (DuPont control)

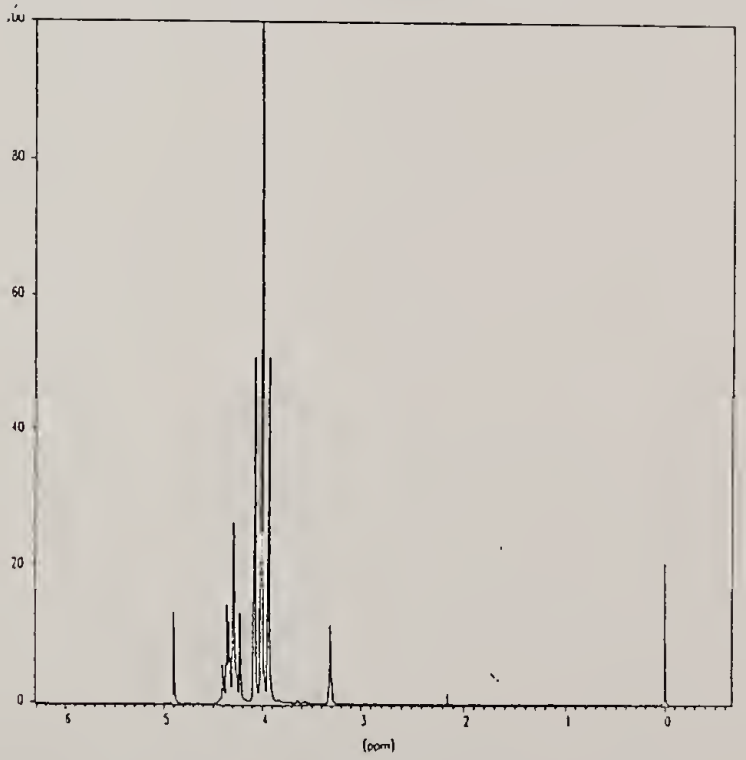


Figure 7.8: NMR of FBS

Table 7.1: Composite mixtures

	range of concentraions
polymer	3-6 wt%
silane	0.5-3.0 wt%

Table 7.2 shows the limits determined for the system that did not show cloudiness due to phase separation. This system did pass the clarity check, however, the coating quality was questionable. By using a simple thumbnail scratch test, the material deformed easily and did not adhere to the glass surface nearly as well as the fluoropolymer alone.

Table 7.2: SF-50 + FBS in PP11 miscibility

3 wt% SF-50	0.5-4.5 wt% FBS
4 wt% SF-50	0.5-4.0 wt% FBS
5 wt % SF-50	0.5-3.0 wt% FBS

Conclusion

The nanocomposite technology for fluoropolymers is a very new and relatively unexplored field. Adopting a sol-gel route within the fluorinated media required for miscibility is difficult due to the lack of control over the reaction. Two different fluoroalkoxy silane systems were developed at DuPont and tested in this laboratory. The results show some promise for one system involving a fluorobutoxysilane and SF-50. However, the product is a homogeneous rubbery material, as opposed to the desired glass network reinforced fluoropolymer. In fact, the system is more rubbery than the

fluoropolymer alone. The most likely cause for this alternate product is that the fluorobutoxy silane reacted to form polysilicates instead of a network structure. Polysilicates having fluorobutoxy side groups would be very rubbery and lend to the product characteristics described. Due to the limitation of dilute systems, the coating product was very thin and physical characterization was not available.

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CHAPTER 8

SUMMARY AND FUTURE INTERESTS

Summary

Fluoropolymers, like FEP copolymers, are very valuable materials due to their chemical stability and low surface energy. Their usage, however, has been limited by the high energy processing required to work with them. After the recent introduction of a new FEP copolymer, SF-25, a whole new field of solution processing has opened up for FEP. The systems initially introduced, SF-25 in PP11, had very limited mixing at 1.6 wt % polymer in solvent. After observing solution formation behavior and the rare gelling phenomenon exhibited by these systems, a novel processing scheme was developed in this laboratory. The breakthrough enabled single application FEP coatings on various substrate materials in the thickness range of 50nm-100μm.

Afterward another FEP copolymer, SF-50, was introduced which is more soluble. Solution processing was utilized to form coating materials for SF-25, SF-50 and Teflon® AF 1601 (a new amorphous fluoropolymer), and the resultant films were compared as to physical properties and coating performance.

The material properties investigated included mechanical properties, thermal properties, and degree and nature of crystallinity. The work revealed that the new FEP copolymers are mechanically as good as the commercial grades of FEP available. The thermal properties, however, are what was compromised to enable solubility. The melting points and glass transition temperatures were all reduced 50-80°C. The thermal behavior

changes can be attributed to a higher degree of disorder exhibited in the hexagonally packed crystal structure of the helical chains.

The coating properties investigated include adhesion, permeability, and corrosion resistance. The adhesion quality is unexpectedly very good for the FEP copolymers and the coatings withstood defect introduction, low temperatures, and stress conditions that were mechanically aggravated. This behavior can be easily traced back to the low coating stresses for these films measured by holographic interferometry. The Teflon® AF 1601, however, is very highly stressed as a coating. Therefore, the smallest defect or slightest agitation caused adhesion failure, or delamination.

The permeability data measured on the new films for standard permeants showed better behavior than what is given for commercial FEP. The primary factor for this phenomenon is that higher densities have been measured for the new films compared to the commercial FEP. The solution processing most likely allows film formation that is relatively free of microvoids, which are a big contributor to enhanced permeation. The corrosion resistance study shows that the new coatings are comparable to existing fluoropolymers at room temperature. However, the lack of data in this area for FEP materials does not allow much direct comparison. Also, as the films are brought above their glass transition temperatures the corrosion resistance suffers dramatically.

One final area of nanocomposite formation was investigated due to the new opportunity the solution media presented, and also because the original expectation was that the adhesion would need improvement. The fluoropolymer solutions were coupled with sol-gel science to try to create an SiO_2 network with fluoropolymer interpenetration. The fluoroalkoxy silane based sol-gel reaction was successful in and of itself. However,

when the fluoropolymer was introduced, incomplete network formation either caused precipitation of small SiO_2 clusters or formation of an alternate polysilicate structure. The precipitation caused visible turbidity in the drying films, while the polysilicate structure caused the composite structure to become very rubbery with poor adhesion.

Future Interests

There are many new branches of research that could stem from this investigation. The solution behavior of these fluoropolymers and its dependence on copolymer content and conditions is worthy of investigation. Also, the gelation behavior could be investigated more thoroughly by x-ray analysis of the gels to obtain microcrystal or bundle structure and NMR of the chain structure to understand the conformation which lends to such behavior.

The anti-reflective capabilities of the materials could be explored in more detail. This would require optical analysis and focus on thin film coatings. Also, the dielectric properties may be affected by the different copolymer content. This area could be investigated with the new solution processing methods to form coatings. There may be potential for interlayer dielectrics.

As stated earlier, the fluorinated sol-gel approach to forming nanocomposites is very new. Further work on silane structure variation and polymer structure variations (through copolymer ratio) can be studied. If the true SiO_2 network can be formed with a fluoropolymer trapped in the pores, the impact on the fluoropolymer coatings industry would be huge. However, the fluoropolymer solutions may already provide such composite structures at surfaces of ceramics. If the flouropolymer is solution coated onto

a porous ceramic, the viscosity of the solutions can get low enough to cause the polymer to infuse the ceramic.

The potential for applications of these fluoropolymer coatings is very large. Continued research in this field would streamline the possibilities and bring the benefit of this technology into the forefront of the commercial market for fluoropolymer coatings.

APPENDIX

APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: FLUOROPOLYMER DISPERSIONS

APPLICANTS: MEREDITH L. WHITE and RICHARD J. FARRIS

"EXPRESS MAIL" Mailing Label Number EM518285341US

Date of Deposit June 24, 1997

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Lisa G Gray

Lisa G Gray

FLUOROPOLYMER DISPERSIONS

Background of the Invention

The invention relates to fluoropolymer dispersions in perfluorinated solvents and their use in the deposition of fluoropolymer coatings.

Poly(tetrafluoroethylene) (PTFE) and its copolymers are highly chemical-resistant and are insoluble in nearly all industrial solvents, qualities that make them desirable for use in harsh environments. An example of such a copolymer is shown in Fig. 1; the figure depicts fluoro-ethylene-propylene (FEP), a copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP). The TFE and HFP monomers are also indicated in Fig. 1. Commercial preparations of FEP are available that contain varying TFE:HFP ratios. For example, TEFLON® FEP100 (DuPont, Wilmington, DE) is 87 mol % TFE and 13 mol % HFP.

A high molecular weight is generally required for PTFE, FEP, and other TFE copolymers to have sufficient toughness and useful overall mechanical properties (e.g., tensile strength in the range of 7 to 28 MPa). Polymers of molecular weight 1×10^6 to 1×10^7, for example, are suitable for most applications. The melt viscosities of even low molecular weight (e.g., 1×10^5 to 5×10^5) grades of FEP are relatively high and require high power extruders or injection molders to achieve acceptable flow rates. The high molecular weight grades of FEP are very difficult to process, requiring high pressures and temperatures for extrusion.

Early solubility studies reported the plasticization of 1-2% PTFE at 290-310°C in high molecular weight solvents, such as perfluorokerosenes and other perfluorinated oils. It was predicted that a larger melting point depression

would occur for solvents of lower molecular weight and that plasticization should therefore occur at lower temperatures in low molecular weight solvents (Smith et al., *Macromolecules*, 18:1222-1228, 1985).

However, low molecular weight solvents also have low boiling points, leading to the conclusion that high pressures would be necessary (i.e., to increase the boiling point of the solvent) if low molecular weight solvents were to be used. The PTFE solubility investigation was therefore extended to other perfluorocarbon solvents in enclosed vessels at higher pressures using a low molecular weight PTFE (Tuminello et al., *Macromolecules*, 27:669-676, 1994).

DuPont researchers discovered that a TEFLON® FEP containing 75 mol % TFE and 25 mol % HFP can be dissolved in perfluoro(decahydrophenanthrene) by combining the components at room temperature, then heating to 175°C (i.e., reflux conditions) with stirring to obtain the solution. The highest concentration of the 75:25 FEP obtained by this method was 1.6 wt % solids; more highly concentrated mixtures gelled irreversibly upon cooling from the solution formation temperature of 175°C (U.S. Pat. No. 5,266,639 to Chapman Jr., et al.).

Summary of the Invention

The invention is based on the discovery that copolymers of tetrafluoroethylene (TFE) and certain other fluoropolymers are partially miscible with perfluorinated solvents at relatively low temperatures and ambient pressures. This discovery has applications, for example, in the manufacture of highly chemical- and friction-resistant fluoropolymer coatings. Coatings ranging in thickness from 50 nm to 100 μm can be made via a single application of the new copolymer dispersions.

One aspect of the invention features a dispersion including a perfluorinated solvent and a copolymer of tetrafluoroethylene and hexafluoropropylene dispersed in the solvent. The concentration of the copolymer in the dispersion is at least 3% by weight at atmospheric pressure. In certain embodiments, the concentration can be at least 5% or at least 10% by weight at atmospheric pressure.

The ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer can be, for example, between 5:1 and 4:6, between 4:1 and 1:1, or between 3:1 and 1:1. The perfluorinated solvent can be, for example, perfluoro(decahydrophenanthrene).

Another aspect of the invention is a method for preparing a dispersion of a fluoropolymer. The method includes the steps of combining the fluoropolymer and a perfluorinated solvent to form a mixture and heating the mixture at a rate of 1 to 5°C per minute up to the temperature at which the mixture becomes optically clear.

In certain embodiments of the method, the concentration of the fluoropolymer in the mixture is at least 3%, at least 5%, or at least 10% by weight at atmospheric pressure.

The fluoropolymer can be, for example, a copolymer of tetrafluoroethylene and hexafluoropropylene, a copolymer of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole, or a copolymer of tetrafluoroethylene and perfluoropropyl vinyl ether. When a copolymer of tetrafluoroethylene and hexafluoropropylene is used, the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer can be, for example, between 5:1 and 4:6, between 4:1 and 1:1, or between 3:1 and 1:1.

The perfluorinated solvent can be, for example, perfluoro(trihexylamine), perfluoro(dibutylmethylamine),

perfluoro(2-n-butyltetrahydrofuran), hexafluorobenzene, perfluoro(decahydrophenanthrene), an oligomer of perfluoro(decahydrophenanthrene).

Still another aspect of the invention is the dispersion formed by any embodiment of the described method.

Yet another aspect of the invention is a method of coating a substrate with a fluoropolymer. The method includes the steps of contacting the substrate with a dispersion of the invention to form the coating, then heating the coated substrate to a temperature sufficient to evaporate the solvent, and, in certain cases, to a temperature sufficient to anneal the coating.

The "contacting" step can, for example, include spin coating, blade drawing, or dip coating.

The method can also include the step of removing the substrate from the coating to form a thin film.

"Partially miscible," when used to refer to copolymers and solvents, means that when copolymers are combined with the solvents according to the methods described herein, the result is an optically clear mixture wherein the finely ground copolymer powder is swollen by the solvent.

Although the term "dispersion," in common usage, is defined as "a suspension . . . of solid, liquid, or gaseous particles, of colloidal size or larger, in a liquid, solid, or gaseous medium" (American Heritage Dictionary, Second College Edition), it is used herein to represent solutions as well as suspensions. The dispersions of the invention exhibit properties of both solutions (e.g., optical clarity) and suspensions (e.g., cloudiness), depending on numerous parameters such as temperature, stirring rate, concentration, and composition.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patents, manufacturers' technical information, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present application, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

The new dispersions and methods provide numerous advantages. For example, polymers containing 25-50 mol % HFP, including those having high molecular weight, can be used as coatings for space vehicles and satellites, or the tiles of the space shuttle, for example. Furthermore, the coatings prepared by the new methods exhibit homogeneity, have excellent adhering qualities, and require no surface modification for most substrates.

The new methods are energy- and cost-efficient. The coatings reduce friction and corrosion, thus causing less energy to be dissipated as heat. The equipment and energy required to heat the dispersions to 50°C and to dry the coatings (i.e., to remove residual solvent) can be much less costly than those required for melt processing.

The new methods also allow preparation of thinner coatings than are generally attainable with melt processing or spraying of aqueous dispersions. Nevertheless, the new methods also enable one-step formation of coatings ranging in thickness from 50 nm to 100 μm, without requiring multiple layers to achieve greater thickness. Indeed, once

the entire substrate surface has been completely covered with a fluoropolymer coating, the coating cannot be further built up in thickness; the dispersion does not stick to the dried, coated surface. Thus, the new methods produce thicker coatings that provide improved barrier properties. Additionally, the solvent can be recycled after the coating procedure.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

Brief Description of the Drawings

Fig. 1 is a structural formula of an FEP copolymer, indicating the TFE and HFP monomer units.

Fig. 2 is a plot of solution behavior of various concentrations of an FEP containing a 75:25 TFE:HFP ratio in perfluoro(decahydrophenanthrene).

Detailed Description

Dispersions of tetrafluoroethylene (TFE) copolymers, such as fluoro-ethylene-propylene (FEP) copolymers (Fig. 1), in perfluorinated solvents can be prepared at relatively low temperature and ambient pressure. The dispersions can be cooled to room temperature and reheated repeatedly; the dispersions consistently become clear upon reheating. The dispersions can be used, for example, in the preparation of fluoropolymer-coated materials.

Polymers and Solvents

Numerous perfluorinated solvents can be employed in making the new dispersions. Many are commercially available. For example, perfluoro(decahydrophenanthrene) is sold by Rhône-Poulenc (Princeton, NJ) under the trade name

Flutec PP11™; it is also sold by, for example, PCR, Inc. (Gainesville, FL). Perfluoro(trihexylamine), perfluoro(dibutylmethylamine), and perfluoro(2-n-butyltetrahydrofuran) are sold by 3M (St. Paul, MN) under the trade names FC-71™, FC-40™, and FC-75™, respectively. Hexafluorobenzene is available from Aldrich (Milwaukee, WI). Derivatives of these solvents can be used, as well. For instance, oligomers of PP11™ have been described by Tuminello et al. (*Macromolecules*, 27:669-676, 1994). Other solvents having various functional groups (e.g., ethers, perfluoroalkyls, other haloalkyls, and sulfides) can also be used.

A wide variety of polymers and copolymers can also be used in preparing the dispersions. For example, an FEP having a 75:25 TFE:HFP ratio (prepared according to U.S. Pat. No. 5,266,639 to Chapman, Jr. et al.) was investigated, as was an FEP having a 50:50 TFE:HFP ratio (prepared according to U.S. Pat. No. 5,478,905 to Anolick et al.). Other FEPs, having TFE:HFP ratios ranging from 5:1 to 4:6, can also be prepared according to the methods described in the Chapman and Anolick patents. Copolymers of TFE with 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) are available from DuPont (Wilmington, DE) under the tradename TEFLON® AF. Copolymers of TFE with perfluoropropyl vinyl ether (PPVE) are described by Tuminello (*Macromolecules*, 28:1506-1510, 1995). Other derivatives of these copolymers, wherein one or both components have been replaced, can also be employed in the preparation of dispersions.

Preparation of the Dispersions

Mixtures containing Flutec PP11™ and up to 12 weight % of the 75:25 FEP are heated slowly (i.e., over about 30 minutes) to 50-60°C. After about thirty additional

minutes of stirring at this temperature, the mixtures become homogeneous, optically clear, and the particles that make up the copolymer become swollen. For the 50:50 FEP, the dispersions need to be heated to about 100°C before clearing occurs.

The behavior of dispersions containing 1-12 weight % of the 75:25 FEP in Flutec PP11™ is plotted in Fig. 2. The lower curve, indicated by the diamonds, denotes the "clearing" temperature observed visually for each of the mixtures; the clearing temperature is fairly constant (i.e., 50-60°C) irrespective of concentration. The upper curve, indicated by the squares, corresponds to the "critical" temperature, above which a change occurs that causes the mixture to irreversibly gel on cooling. Over a broad range of concentrations, the critical temperature for the 75:25 FEP is around 75°C. The area between the curves indicates the range of processability. As used herein, "processability" refers to uniform flow in a viscosity range that is conducive to practice of the new methods.

If the stirring of the dispersion is discontinued or the dispersion is cooled to room temperature, the mixtures become increasingly viscous and cloudy with time. Room temperature viscosity is proportional to the weight % of the solids in the dispersion. Unexpectedly, however, the liquid-like properties required for processing can be regained by reheating the mixture to 50-60°C with stirring. Optical clarity is also regained. As long as the critical temperatures depicted on the upper curve of Fig. 2 are not exceeded, reversible clearing can be accomplished. 50:50 FEP dispersions become viscous upon cooling to room temperature but do not become cloudy.

Surface Preparation of the Substrates

Most substrates require no surface preparation or modification. For coating aluminum substrates, however, it is necessary to etch the surface with 10M sodium hydroxide for 30 seconds, rinse with water, and wash with acetone prior to coating.

Methods of Using the Polymer Dispersions

Doctor blade drawing

The dispersion can be drawn into a thin film or used to form a thin film on a solid substrate using a doctor blade. The doctor blade is prepared for coating by scraping it with a razor blade to remove contamination or previous build-up, then washing it with acetone. The 75:25 FEP dispersion, for example, is then heated to 50°C with stirring until clear, then an amount sufficient to cover the entire substrate surface is poured along the inside edge of the blade. The blade is drawn down to pull the dispersion across the substrate, leaving a coating of the desired thickness. For example, a 100 μm thick coat can be prepared by loading the doctor blade with 50 ml of a 12 weight % dispersion of the 75:25 FEP.

Spin coating

The 75:25 FEP dispersion is heated to 50°C with stirring until clear. It is then poured onto the center of the substrate. The substrate is spun at 550 rpm for a duration of 1-2 minutes to evenly coat the substrate. The thickness of the coating depends on the speed of rotation; a faster speed results in a thinner coating. With a 3 weight % 75:25 FEP dispersion, evenly distributed coatings as thin as 50 nm can be prepared by spin coating.

With HFP-rich copolymers (e.g., 50:50 TFE:HFP), more dilute dispersions can be prepared that yield thinner

coatings. Evenly distributed coatings are not always a priority, however. For example, in the preparation of nonstick or low friction surfaces, it is not necessary that the entire surface be covered. For such applications, less concentrated dispersions can be used (e.g., 1, 0.1, or 0.01 weight %, or less).

Dip coating

The 75:25 FEP dispersion is heated to 50°C with stirring until clear, then poured into a tall, narrow flask to form a bath. The substrate material is dipped into the bath with a controlled withdrawal speed; a faster withdrawal speed results in a thinner coating.

Drying and annealing

The coated substrate is placed in a convection oven at room temperature. The following temperature profile, for example, can be used to dry and anneal the sample:

Ramp 1-5°C/min to 50°C - hold for 1 hour
Ramp 1-5°C/min to 100°C - hold for 1 hour
Ramp 1-5°C/min to 150°C - hold for 1 hour
Ramp 1-5°C/min to 220°C - hold for 1 hour

The sample is allowed to cool slowly to room temperature.

Drying and annealing are necessary to ensure that all of the solvent is evaporated and that the surface coating is evenly distributed. Annealing causes the coating to flow from regions of thick coating to regions of thin coating, thereby reducing stress within the coating.

Applications of the Coatings

The coatings obtained from the new methods have remarkable adhesion energy when coated on various metals and glasses and will not delaminate if defects are introduced. They are clear films that can be used in anti-reflective

applications such as on television screens, computer screens, or oven doors.

The barrier properties of the coatings produced from the new dispersions or new methods are much improved relative to those reported for FEPs currently available (e.g., TEFLON® FEP100), based on the results of permeability and corrosion testing. For example, the new coatings are less permeable to carbon dioxide and to compressed air than TEFLON® FEP100 coatings of similar thickness. These properties are probably due, at least in part, to decreased density resulting from a lower degree of porosity from the new methods. The mechanical properties are equivalent to or higher than those of TEFLON® FEP100, with a modulus of 0.70 to 0.75 GPa resulting from tensile testing of the new coating, compared with 0.60 to 0.70 GPa for TEFLON® FEP100.

Free standing films in the thickness range mentioned can be obtained by etching away the aluminum or copper substrates. Aluminum is etched by aqueous 10M sodium hydroxide, which does not penetrate the FEP coating. Copper can be etched by aqueous copper(II) chloride/hydrochloric acid solutions. The films can be used as barrier membranes.

The new dispersions are exceptionally effective for coating porous substrates such as ceramics, because the dispersions are of sufficiently low viscosity that they can permeate the pores of the substrate. The treatment of porous ceramics finds utility, for example, in the coating of tiles for use on the outer surface of spacecraft. The new coatings make the ceramic tile surfaces hydrophobic and thus prevent penetration of the surface by water. It is necessary that the tiles remain dry during the entry of the spacecraft into the freezing temperatures encountered on the voyage into outer space.

Thin fluoropolymer films can also have applications as nonstick coatings, dielectric coatings, low friction coatings, melt adhesive coatings, or protective coatings. For example, a thin coating can be applied to magnetic data storage media to afford durability and protection.

Examples of substrates that can be coated include, but are not limited to, metals, semiconductors, glass, carbon or graphite, polymers, films, paper, foils, sheets, slabs, wafers, wires (e.g., catheter wire guides, brake cables and other push-pull actuating wires, and electrical wires), fibers, filaments, cylinders, spheres, irregularly and regularly shaped objects, screens, foams, porous and non-porous substrates, fabrics, engine parts, razor blades, containers, belts, rods, tubes, bolts, nuts, screws, and other fasteners, gaskets, o-rings, seals, and membranes.

The invention will be further described in the following examples, which do not limit the scope of the invention described in the claims.

EXAMPLES

Example 1

19.4 g of Flutec PP11™ solvent (Rhône-Poulenc, Princeton, NJ) was weighed out into a flask. 600 mg of DuPont (Wilmington, DE) 75:25 FEP powder (prepared according to U.S. Pat. No. 5,266,639 to Chapman, Jr. et al.) was added to the solvent. The components were mixed initially by shaking, then the flask was clamped in a room temperature water bath on a magnetic stir plate.

The water bath was slowly heated to about 50°C while the mixture was vigorously stirred. Clearing of the mixtures was observed under these conditions. Some of the mixture was processed immediately. The remainder was allowed to cool and was stored at room temperature. When it

was necessary to use the remainder, it was stirred and reheated, without the temperature's being allowed to exceed 60°C. When the mixture became clear, it was processed.

Coatings were obtained by spin coating five different substrates (i.e., tin, steel, aluminum, copper, and glass) with the 12 weight % dispersion made in Example 1 and dispersions of other concentrations ranging from 4 to 15 weight % copolymer. Substrates ranging in size from 2 cm x 2 cm to 10 cm x 10 cm were spun at 550 rpm for 1-2 minutes with 2-4 ml of the dispersion. After spin coating, the samples were annealed in a vacuum oven according to the following temperature profile:

Ramped 2.5°C/min to 50°C - hold for 1 hour
Ramped 2.5°C/min to 100°C - hold for 1 hour
Ramped 2.5°C/min to 150°C - hold for 1 hour
Ramped 2.5°C/min to 220°C - hold for 1 hour

The sample was allowed to cool slowly to room temperature. The resultant coating was transparent and adhered well to the substrate.

Coatings from dispersions containing less than 3 weight % FEP were found to be inhomogeneous and nonuniform by optical interference studies. Thus, the advantage of being able to use higher concentrations of FEP is quite important, because it yields uniform coatings.

Free-standing films were made by removing the FEP coating from the substrate. A 4 weight % dispersion gave a film 2 μm thick after spin coating, a 10 weight % dispersion gave a film 7.5 μm thick, and a 15 weight % dispersion gave a film 12 μm thick.

Example 2

A vat, sized to accommodate a substrate, such as a mechanical part, a wire, a fiber, a pan, or a window, is obtained. The vat is equipped with stirring and heating apparatuses that maintain the temperature of the vat's contents at around 50°C. A dispersion of a copolymer of TFE and PDD in hexafluorobenzene is added to the vat. The concentration of the dispersion is chosen to give the desired thickness required for a single coating application. Samples are dip coated and subsequently annealed, then slowly cooled to room temperature. The solvent is recovered and recycled.

Example 3

The dispersion of Example 1 is painted onto an object to protect its surface. After annealing and drying, the coated object is used as desired. When the coating becomes worn due to excessive wear or misuse, the object is repainted or spot repaired with additional dispersion.

Example 4

A cotton jacket is dip coated in a dispersion containing a copolymer of TFE and PPVE in perfluoro(2-n-butyltetrahydrofuran to produce a lightweight water-repellant raincoat.

Other Embodiments

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects,

advantages, and modifications are within the scope of the following claims.

For example, it is possible to make fluoropolymer thread by solution fiber-spinning. Solution fiber-spinning is a process in which a thread of the polymer is pulled from a fairly concentrated dispersion as a continuous string. The thread is then drawn into a fiber and the solvent is driven out by heating or by submerging the fiber in a liquid that is immiscible with both the fiber and the solvent (e.g., water). The resulting fiber can be taken up onto a spool and, for example, woven into a fabric.

What is claimed is:

1. A dispersion comprising a perfluorinated solvent and a copolymer of tetrafluoroethylene and hexafluoropropylene dispersed in the solvent; wherein the concentration of the copolymer in the dispersion is at least 3% by weight at atmospheric pressure.

2. The dispersion of claim 1, wherein said concentration is at least 5% by weight at atmospheric pressure.

3. The dispersion of claim 2, wherein said concentration is at least 10% by weight at atmospheric pressure.

4. The dispersion of claim 1, wherein the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer is between 5:1 and 4:6.

5. The dispersion of claim 1, wherein the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer is between 4:1 and 1:1.

6. The dispersion of claim 1, wherein the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer is between 3:1 and 1:1.

7. The dispersion of claim 1, wherein said perfluorinated solvent comprises perfluoro(decahydrophenanthrene).

8. A method for preparing a dispersion of a fluoropolymer, the method comprising:

combining the fluoropolymer and a perfluorinated solvent to form a mixture;

heating the mixture at a rate of 1 to 5°C per minute up to the temperature at which the mixture becomes optically clear, to form a dispersion.

9. The method of claim 8, wherein the concentration of the fluoropolymer in the mixture is at least 3% by weight at atmospheric pressure.

10. The dispersion of claim 9, wherein said concentration is at least 5% by weight at atmospheric pressure.

11. The dispersion of claim 10, wherein said concentration is at least 10% by weight at atmospheric pressure.

12. The method of claim 8, wherein said fluoropolymer is selected from the group consisting of a copolymer of tetrafluoroethylene and hexafluoropropylene, a copolymer of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole, and a copolymer of tetrafluoroethylene and perfluoropropyl vinyl ether.

13. The method of claim 8, wherein said fluoropolymer comprises a copolymer of tetrafluoroethylene and hexafluoropropylene.

14. The dispersion of claim 13, wherein the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer is between 5:1 and 4:6.

15. The dispersion of claim 13, wherein the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer is between 4:1 and 1:1.

16. The dispersion of claim 13, wherein the ratio of tetrafluoroethylene to hexafluoropropylene in the copolymer is between 3:1 and 1:1.

17. The method of claim 8, wherein said perfluorinated solvent is selected from the group consisting of perfluoro(decahydrophenanthrene), an oligomer of perfluoro(decahydrophenanthrene), perfluoro(trihexylamine), perfluoro(dibutylmethylamine), perfluoro(2-n-butyltetrahydrofuran), and hexafluorobenzene.

18. The method of claim 8, wherein said perfluorinated solvent comprises perfluoro(decahydrophenanthrene).

19. A dispersion prepared by the method of claim 8.

20. A method of coating a substrate with a fluoropolymer, the method comprising contacting the substrate with the dispersion of claim 1 to form the coating, and heating the coated substrate to a temperature sufficient to evaporate the solvent.

21. The method of claim 20, further comprising heating the coated substrate to a temperature sufficient to anneal the coating.

22. The method of claim 20, wherein said contacting step comprises a coating technique selected from the group consisting of spin coating, blade drawing, and dip coating.

23. A method of forming a thin film, the method comprising contacting the substrate with the dispersion of claim 1 to form the coating, heating the coated substrate to a temperature sufficient to evaporate the solvent, and removing the substrate from the coating to form the film.

24. A method of coating a substrate with a fluoropolymer, the method comprising contacting the substrate with the dispersion of claim 19 to form the coating, and heating the coated substrate to a temperature sufficient to evaporate the solvent.

25. The method of claim 24, further comprising heating the coated substrate to a temperature sufficient to anneal the coating.

26. The method of claim 24, wherein said contacting step comprises a coating technique selected from the group consisting of spin coating, blade drawing, and dip coating.

27. A method of forming a thin film, the method comprising contacting the substrate with the dispersion of claim 19 to form the coating, heating the coated substrate to a temperature sufficient to evaporate the solvent, and removing the substrate from the coating to form the film.

FLUOROPOLYMER DISPERSIONS

Abstract of the Disclosure

The invention is based on the discovery that copolymers of tetrafluoroethylene (TFE) and certain other fluoropolymers are partially miscible with perfluorinated solvents at relatively low temperatures and ambient pressures. This discovery has applications, for example, in the manufacture of highly chemical- and friction-resistant fluoropolymer coatings. Coatings ranging in thickness from 50 nm to 100 μm can be made via a single application of the new copolymer dispersions.

One aspect of the invention features a dispersion including a perfluorinated solvent and a copolymer of tetrafluoroethylene and hexafluoropropylene dispersed in the solvent. The concentration of the copolymer in the dispersion is at least 3% by weight at atmospheric pressure.

Another aspect of the invention is a method for preparing a dispersion of a fluoropolymer. The method includes the steps of combining the fluoropolymer and a perfluorinated solvent to form a mixture and heating the mixture at a rate of 1 to 5°C per minute up to the temperature at which the mixture becomes optically clear.

247888.B11

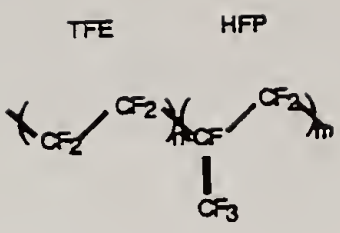
TFE
HFP
CF2
CF2
CF2
CF
CF3

Fig. 1

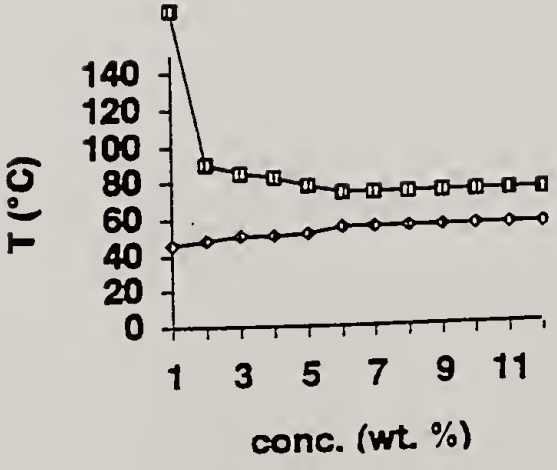
T (°C)
140
120
100
80
60
40
20
0
1
3
5
7
9
11
conc. (wt. %)

Fig. 2

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